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Inter-Industry Collaborative Study of the Toxicity Characteristic Leaching Procedure Addendum to Compilation of Phase 1A and Phase 2 Data

Lancy International, Inc., Zelienople, PA

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Lancy International, Inc.
525 West Castle Street
P.O. Box 490
Zelienople, PA 16063

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INTER-INDUSTRY COLLABORATIVE STUDY
of the
TOXICITY CHARACTERISTIC LEACHING PROCEDURE

Addendum to

COMPILATION OF PHASE IA AND PHASE II DATA

September 15, 1986

Sponsoring Organizations:
American Iron and Steel Institute
American Mining Congress
American Textile Manufacturers Institute
Chemical Manufacturers Association
Lead Industries Association
Utility Solid Waste Activities Group

Participating Laboratories:
Envirodyne Engineers, Inc.
St. Louis, MO
IT Corporation
Pittsburgh, PA
PEI Associates, Inc.
Cincinnati, OH
Radian Corporation
Austin, TX
Rocky Mountain Analytical Laboratory
Arvada, CO
Western Research Institute
Laramie, WY

Technical Coordinator:
Environmental Services Division
Lancy International, Inc.
Zelienople, PA

LANCY ENVIRONMENTAL SERVICES
DIVISION OF LANCY INTERNATIONAL, INC
An Allied Separation Technology Company

525 West New Castle Street P.O. Box 490 Zelienople, Pennsylvania 16063 Telephone 412 452 9361

TC
LCC

September 17, 1986

RCRA Docket
U.S. Environmental Protection Agency
401 M Street, S.W.
Washington, D.C. 20460

Ref: Docket Number F-86-TC-FFFFF

Enclosed is the final report and three copies of the Inter-Industry Collaborative Study of the Toxicity Characteristic Leaching Procedure, as included in the Environmental Protection Agency proposed rule amending 40 CFR 261 (51 Federal Register 21648, June 13, 1986). This report acts as an addendum to the Inter-Industry Group's Compilation of Phase IA and II Data, submitted to this docket on August 12, 1986.

Respectfully submitted,

Connie Glover

Connie Glover
Manager
Lancy Environmental Services Division
Lancy International, Inc.

Enclosures

EXECUTIVE SUMMARY

The Inter-Industry TCLP Group was formed in 1985 by six trade associations representing a broad cross-section of industry to evaluate the new solid waste leaching procedure under development by EPA. A collaborative study of the Toxicity Characteristic Leaching Procedure (TCLP) sponsored by this group has recently been completed. Six laboratories participated in the study, providing data which were submitted collectively as comment to Docket Number F-86-TC-FFFFF on August 12,1986. This report is an addendum to that submittal.

The goals of the study were:

- to compare the proposed TCLP and the EP Toxicity test on wastes of interest to the sponsoring associations,
- to estimate the precision and reliability of the TCLP, and
- to identify procedural problems in the TCLP.

The study was conducted in two phases, a familiarization phase and a second phase constituting the majority of the test program. In the first phase, comparative TCLP and EP Toxicity tests were run on five industry wastes and one composite spiked waste. Analyses focused on inorganic parameters since the Zero Headspace Extractor (ZHE) was not yet available.

The second phase consisted of four test series: a TCLP precision study, characterization of wastes by the TCLP, a comparison of TCLP and EP Toxicity, and a comparison of deionized water and acetate medium in the TCLP test. Fifteen wastes supplied by the sponsoring associations were tested. Waste-specific sampling instructions and a laboratory protocol were developed for this study. EPA methodology was employed for all anayses which consisted of seven of the eight "EP metals" and both volatile and semi-volatile organics from the proposed Toxicity Characteristic list. Data were supported by the full quality assurance programs of the participating laboratories. Duplicate determinations were made on all samples and "total method spikes" were employed for selected inorganic and organic parameters.

Results of the collaborative study, presented in this report, indicate that the TCLP and EP Toxicity are similar in precision. The relative standard deviations for both tests range from approximately 10% to 100% depending upon waste type and parameter measured. Intra-laboratory precision was found to be considerably better than inter-laboratory precision. The TCLP produced somewhat higher leachate concentrations than did the EP in this study. Problems were identified in the use of the ZHE. Carry-over of contaminants from one extraction to another is one of the most serious problems. In general, TCLP results were found to have an average uncertainty of ±100% (based on ±3 standard deviations), with much of the variability of results attributed to waste-specific factors.

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1.0 INTRODUCTION

The Toxicity Characteristic Leaching Procedure (TCLP), proposed by EPA to replace and expand upon the current EP Toxicity test, has been evaluated in a study sponsored by the Inter-Industry TCLP Group, comprised of the trade associations listed on the first page of this document. The data obtained in the study and submitted August 12,1986 as comment to Docket Number F-86-TC-FFFFF were produced by six participating laboratories, also listed on the first page of this document. Lancy Environmental Services Division, Lancy International, Inc provided technical coordination of the study and prepared this report.

This addendum to the submittal of comments to Docket Number F-86-TC-FFFFF referenced above includes a description of the test program conducted (including a description of the wastes tested), statistical evaluation of those data for which such manipulation is appropriate, commentary on the results, and discussion of various aspects of the TCLP test procedure based on the experience of the participating laboratories. This document deals only with technical and practical issues related to the TCLP and does not address the regulatory aspect of the proposed rule. No discussion is included on the appropriateness of regulatory levels proposed for the TCLP leachate except as they are influenced by constraints of the test procedure, based on data from this study.

In evaluating the available data and organizing this discussion, the original goals of this program were followed, which were:

- to compare the proposed TCLP and the EP Toxicity tests on wastes of interest to the sponsoring associations,
- to estimate the precision and reliability of the TCLP, and
- to identify procedural problems in the TCLP.

This report references the data package entitled "Inter-Industry TCLP Study, Compilation of Phase IA and Phase II Data" dated August 8, 1986, which was included in the August 12 submittal to Docket Number F-86-TC-FFFFF and serves as an addeddum to that submittal. The original data are not repeated here. The tables of reduced data in this document were prepared from the data in that original submittal. Since the submittal of the original data package, a few corrections have been made. These are shown as errata in Appendix A.

2.0 TEST PROGRAM

Originally, the study was scheduled to be conducted in two phases, the first being a familiarization program, with test work beginning one month after a Zero Headspace Extractor (ZHE) device with at least tentative EPA approval was available and with a projected Phase II completion date of December 20, 1985. When it became apparent that ZHEs would not be available to meet that timetable, the schedule was moved ahead and then revised to begin with a Phase IA, a familiarization phase for all aspects of the TCLP except the procedure for volatiles, which requires the ZHE. This phase was initiated in October, 1985, utilizing what was then an unpublished draft version of the TCLP obtained from EPA. Once the TCLP was published in the Federal Register on January 14, 1986 and the raw data from Phase IA were available by January 20, 1986, planning for Phase II began. Some of the Phase IA data were submitted as part of comments on Docket No. LDR-2, the proposed land disposal ban regulations, which contained the TCLP.

Phase II, including a precision study and comparison of the TCLP and EP Toxicity tests, was delayed until (1) ZHEs were available and (2) the toxicity characteristic was proposed in the Federal Register, including the new list of contaminants and regulatory levels (June 13, 1986). The latter information was necessary to complete the design of the study. The majority of data from Phase II were available, i.e. had been reported by the laboratories, by August 3, 1986.

The following sections describe the two phases in more detail.

2.1 Phase IA

The objectives of this phase were:

- o Familiarization with TCLP
- o Preliminary comparison of TCLP and EP
- o Identification of procedural problems
- o Development of information for comment to EPA
- o Preliminary assessment of TCLP on industry wastes
- o Collection of information for use in planning the remainder of the project

Phase IA consisted of comparative testing of the EP and TCLP without the ZHE by six laboratories. One waste (identified as #6) was prepared in Lancy's laboratory for distribution of a subsample to each of the six laboratories. Five other wastes contributed by member companies of the sponsoring associations were tested. Both sampling protocols and laboratory protocols were developed for this phase of the study. Standardized forms were provided for submitting data and comments (See Appendices B and C). The EPA draft TCLP dated October 4, 1985 and the EP Toxicity test identified as Method 1310 in SW 846, 2nd ed, revised, were used for this study. Samples were run in duplicate.

2.1.1 Phase IA Wastes Tested

The wastes tested in Phase IA are shown in Table 1.

TABLE 1 - PHASE IA WASTES

Description
Copper slag from a copper smelting reverb furnace.
Waste from styrene production reactor bottoms.
Waste activated sludge from treatment of a woven fabric finishing plant waste.
Dust from an arc furnace used to produce steel.
Dry sludge from treatment of various waste water streams from an electric utility.
Composite waste (Waste #6).

Waste #6 was prepared from a composite of two actual waste samples known to contain various metals and was "spiked" with organic compounds in the cresol and phenol families in an attempt to produce a uniform homogeneous material which could be split among laboratories and which was known to contain organics which appeared on EPA's tentative list of TCLP parameters in the semi-volatile fraction.

The procedure used for preparation of waste #6 is described below:

3.0 Kg of baghouse dust from a steelmaking operation was combined with 1.0 Kg of sinter waste from a lead smelting facility. 1.0 liter of ACS grade methylene chloride, spiked with 1.0 ml of m-cresol and 0.5 ml pentachlorophenol, was added to the 4.0 Kg of dry combined waste. The resulting slurry was thoroughly mixed and spread to a uniform depth of approximately 4 cm in a rectangular polypropylene container. The container was gently heated at low temperature on a hot plate to evaporate the solvent, and the resultant dry material was split as follows.

The waste was mixed by making ten passes along both the X and Y axes with a trowel and turning one thickness of material (4 cm) over with each pass across the surface area of the waste. The container was shaken by hand in a reciprocating manner ten times. The sample was flattened with a straight edge and divided into quarters. A 20 g portion was transferred from each quarter to each of eight (8) 1 liter glass jars. The mixing and splitting procedure was repeated five (5) additional times, resulting in 8 sub-samples of approximately 500 g each. Sample jars were sealed and labeled, six for shipment to the participating laboratories, one for analysis by Lancy, and one for retention.

2.1.2 Test Design

For all wastes, seven inorganic parameters (all of the EP Toxicity metals with the exception of silver) were determined in both TCLP and EP toxicity leachates. Silver was omitted at the request of the sponsoring associations based on their knowledge that the types of wastes to be tested did not contain silver. In addition, even though this was a preliminary familiarization stage, it was intended that at least some organics which had been tentatively identified by EPA for inclusion in the toxicity characteristic be analyzed in TCLP leachates generated in Phase IA. Measurement of organics was intended on those wastes which were expected to contain organics and on waste #6 which had been "spiked", as described above. Technical controversy over the application of EPA methodology for analysis of acid extractable organics to the TCLP leachate matrix was unresolved at the time of Phase IA testing. Measurement of phenols colorimetrically and TOX (both by EPA methods) were substituted for determination of acid extractables.

TABLE 3 - DISTRIBUTION OF PHASE IA SAMPLES

Laboratory #	Waste #
1	2 & 6
2	3 & 6
3	1 & 6
4	5 & 6
5	4 & 6
6	6

2.1.3 Reporting of Results

Laboratories were asked to complete all portions of Phase IA data sheets shown in Appendix C. These data included information on particle size reduction, apparatus used, extraction fluid used, initial and final pH, analytical method, and analyst. QA data were not reported but were retained by each laboratory.

2.2 Phase II

Phase II of the study had four basic objectives:

1) To obtain data on the precision of the TCLP
2) To characterize wastes representative of the industries funding the study
3) To compare TCLP and EP Toxicity data on several wastes
4) To compare data obtained with DI water and the acetate medium in the TCLP procedure

Four series of tests were run in Phase II to accomplish the above objectives. Wastes were supplied by the sponsoring organizations. The following paragraphs provide details on the Phase II activities.

2.2.1 Phase II Wastes Tested

The number of wastes tested in Phase II and the particular waste types were selected by the sponsoring organization. Table 4 gives a brief description of each waste.

TABLE 4 - PHASE II WASTES

Description	Association
Waste activated sludge from a woven fabric finishing mill	ATMI
Floor spill clean-up from a trichloroethylene production facility	CMA
Impounded mine tailings from a precious metals deep mining operation	AMC
Electric arc furnace dust from a steel manufacturing facility	AISI
Impounded mine tailings from an open-pit copper mining operation	AMC
Wastewater treatment sludge from a coal-fired power plant	USWAG
Waste activated sludge from a woolen fabric finishing mill	ATMI
Waste activated sludge from a knit dye and finishing mill	ATMI
Flyash from a coal-fired power plant	USWAG
Wastewater treatment sludge from a lead smelting and battery manufacturing facility	LIA
Floor spill clean-up from a trichloroethylene production facility	CMA
Bottom ash from a coal-fired power plant	USWAG
Wastewater treatment sludge from a steel manufacturing electroplating operation	AISI
Impounded mine tailings from a lead mining operation	AMC
Blast furnace slag from a steel manufacturing facility	AISI

These wastes cover a broad spectrum of industrial waste types. Although due to financial constraints, no compositional analyses were obtained on the specific samples tested in Phase II, the following tables (5 through 12) provide information on typical waste compositions.

TABLE 5 - TYPICAL ANALYSIS OF WASTE # 201

Parameter	Composition
Water	90-95%
Volatile Solids	1-2 %
Suspended Solids	5-10 %
Oxygen Demand, Chemical	30 g/L
Sulfate	<1%
Sulfide	<1% under aerobic conditions

TABLE 6 - TYPICAL ANALYSIS OF WASTE # 204

Parameter	Composition
Total Solids	40%
Oil and Grease	23% of dry solids
Organic Carbon, Total	4% of dry solids
Chromium	0.8% of dry solids

TABLE 7 - TYPICAL ANALYSIS OF WASTE # 206

Parameter	Composition (A)
Density, Kg/M^3	1,430
Flash Point, ^oF	>200
pH (10% slurry)	12.2
Total Solids 103 ^oC	99.9 wt %
Ash Content of Solids, 800 ^oC	99.6 wt % (B)
Alkalinity, as $CaCO_3$	8.5 wt %
Total Cyanide	<0.5 ug/g
Total Phenol	<0.5 ug/g
Total Polychlorinated Biphenyls (PCB's)	<5 ug/g (C)
Total Sulfide	<5 ug/g

	ug/g (B)
Arsenic, As	18
Barium, Ba	4,000
Cadmium, Cd	<2
Chromium, Cr	40
Copper, Cu	54
Lead, Pb	20
Mercury, Hg	0.05
Nickel, Ni	26
Selenium, Se	3.2
Silver, Ag	<2
Zinc, Zn	39

NOTE:
(A) Reported on an "as received" basis unless otherwise noted.
(B) Reported on a "dry weight, (103 ^oC)" basis.
(C) Reported on an "air dried" basis.

TABLE 3 - TYPICAL ANALYSIS OF WASTE # 207

Parameter	Composition (A)
Density, Kg/M^3	1,500
Flash Point, °F	>200
pH (10% slurry)	10.1
Total Solids 103 °C	47 wt %
Ash Content of Solids, 800 °C	93.4 wt % (B)
Total Cyanide	<0.5 ug/g
Total Phenol	<0.1 ug/g
Total Polychlorinated Biphenyls (PCB's)	<1 ug/g (C)
Total Sulfide	25 ug/g
Reactive Sulfide	<5 ug/g
	ug/g (B)
Arsenic, As	11.3
Barium, Ba	1,200
Cadmium, Cd	<2
Chromium, Cr	13
Copper, Cu	14
Lead, Pb	<10
Mercury, Hg	<0.05
Nickel, Ni	8
Selenium, Se	<1
Silver, Ag	<2
Zinc, Zn	6

NOTE:
(A) Reported on an "as received" basis unless otherwise noted.
(B) Reported on a "dry weight, (103 °C)" basis.
(C) Reported on an "air dried" basis.

TABLE 9 - TYPICAL ANALYSIS OF WASTE # 210

Parameter	Composition
Silicon as Si	36 %
Aluminum as Al_2O_3	10 %
Calcium as CaO	39 %
Magnesium as MgO	12 %
Iron as Fe_2O_3	0.5 %
Manganese as MnO	0.9 %
Sulfur	1.4 %

TABLE 10 - TYPICAL ANALYSIS OF WASTE # 211

Parameter	Composition
Iron	30-40 %
Zinc	1-16 %
Lead	1-1.5 %
Silica (SiO_2)	5.3-8.2 %
Calcium as CaO	3.1-4.8 %
Manganese	3.0-5.6 %
Chromium	0.4-10.2 %

TABLE 11 - TYPICAL ANALYSIS OF WASTE # 212

Parameter	Composition
Solids, Total	47 %
Lead	<1 %
Calcium Sulfate	>50 %
Magnesium Sulfate	<1 %

TABLE 12 - TYPICAL ANALYSIS OF WASTE #213

Parameter	Composition (ug/g)
Arsenic	370
Cadmium	8.2
Copper	2,200
Iron	11,800
Lead	600
Manganese	1,200
Silver	10
Zinc	1,490
Sulfur, Total	0.9%

TABLE 13 - TYPICAL ANALYSIS OF WASTE #214

Parameter	Composition (ug/g)
Barium	90
Beryllium	<1
Calcium	94500
Cadmium	<10
Chromium	27
Copper	450
Iron	9950
Potassium	75900
Magnesium	93500
Manganese	1510
Molybdenum	65
Sodium	6610
Nickel	31
Lead	735
Antimony	98
Thallium	<200
Vanadium	6
Zinc	260

Table 14 depicts the distribution of wastes in the overall test plan for Phase II. The choice of parameters to be measured in leachates was based upon the associations' prior knowledge of the waste types.

TABLE 14 - PHASE II PARAMETERS

Wastes		Parameters of Interest		
		Inorganics	Volatiles	Semi-Volatiles
Textile	- 3	X	X	
Chemical	- 2	X	X	X
Utilities	- 3	X		X
Steel	- 2	X		
	- 1	X	X	X
Mining	- 2	X		X
	- 1	X		
Lead	- 1	X		

2.2.2 Test Design

Specific sampling instructions were prepared by Lancy based on information supplied by the associations and the generators. General and site-specific Phase II sampling protocols are shown in Appendix D. Containers, instructions, and general sampling guidelines were shipped to the generators for sampling. Samples were taken by industry personnel at each site and returned to Lancy for homogenization, sample splitting, and distribution. Instructions for wastes which required volatile organics analysis were specific with respect to zero headspace and maintenance of a cold environment for sample collection, storage, and shipment. Pre-cooling of sampling equipment and containers was prescribed.

Samples and completed chain-of-custody forms were received by Lancy. Those which required volatile organic analysis had been shipped in insulated containers with ice packs and were immediately refriger-

ated at <5°C or stored in dry ice. Solid samples were homogenized and split according to ASTM D3987. Liquids were mechanically agitated and split. Samples which required volatile organics analysis were prepared in a "walk-in" refrigeration unit at 6°C to minimize the loss of volatile contaminants. Split samples were labeled, packaged, and shipped to participating laboratories along with laboratory analysis protocol and data reporting packages. Samples which required volatile organics analysis were packed cold with dry ice and shipped by "overnight" carrier.

Each laboratory received general and specific test instructions (See Appendix E). These instructions identified the various types and number of leaching procedures and specific analyses required for each waste. In general, each laboratory received six wastes, with each waste requiring two or three different leaching procedures. Each leaching procedure required triplicate extractions. One of the triplicates was "spiked" prior to extraction with specific analyte solutions prepared and pre-analyzed by Lancy's analytical laboratory. Extract preparation and subsequent analyses were performed using SW-846 Method 1310 for EP Toxicity tests and the June 13, 1986 proposed methodology for TCLP tests. Deionized (DI) water extractions were prepared by following proposed TCLP protocol and substituting DI water as the extraction fluid. Blank preparation and QA/QC requirements were specified in the published methodology and followed for this evaluation. Laboratories which routinely follow EPA's Contract Laboratory Program (CLP) protocol were permitted to substitute CLP QA/QC as a matter of convenience. Analytical Methods used in Phase II are given in Table 15.

TABLE 15 - METHODS OF ANALYSIS - PHASE II

Parameter	EPA Method No.*
Arsenic, Total	7060, 7061
Barium, Total	7080, 6010
Cadmium, Total	7130, 6010
Chromium, Total	7190, 6010
Lead, Total	7420, 6010
Mercury, Total	7470
Selenium, Total	7740, 7741
Metals, Digestion	3010, 3020
Volatile Organics Screen	5030/8240
Volatile Organics	5030/8240
Acid Extractable Organics	3510/8270**
Base/Neutral Organics	3510/8270
EP	1310
TCLP	13(XX)***

*Test Methods for Evaluating Solids Waste
USEPA SW-846 2nd Ed. Revised 04/84
**Use column clean-up procedure as in EPA Collaborative Study
***51 Federal Register 21648, Friday, June 13, 1986/Proposed

A description of each of the four test series in Phase II is given below in Tables 16 through 19. In all cases, laboratories were asked to run test blank determinations as prescribed by the published methodology.

TABLE 16 - Test Series 1: TCLP Precision Study

- o 6 wastes (one from each Association)
- o each waste tested in three (3) labs
- o each test run in duplicate
- o one spike run with each test

Inorganics: (one from each Association)
6 wastes x 3 labs x 2 (dup) = 36
+1 spike for four (4) metals
6 x 3 x 4 = 72

Volatiles: (1 Textile, 1 Chemical, 1 Steel)
3 wastes x 3 labs = 9 samples
screening = 9
analysis = 9 x 2 (dup)
spikes (1/sample/lab) = 9

Semi-Volatiles: (1 Utilities, 1 Mining)
2 wastes x 3 labs x 2 (dup) =12
1 spike/sample/lab = 6

TABLE 17 - Test Series 2: TCLP Waste Characterization

- o 9 wastes (remainder from total of 15)
- o each waste tested in one (1) lab
- o each test run in duplicate
- o one spike run with each test

Inorganics: (2 Textiles, 1 Chemical, 2 Utilities, 2 Steel, 2 Mining)

9 wastes x 1 lab x 2 (dup) = 18
1 spike/waste for four (4) metals: 9 x 4 = 36

Volatiles: (2 Textile, 1 Chemical)

3 wastes x 1 lab = 3 samples
screening = 3
analysis = 3 x 2 (dup)
spikes = 3

Semi-Volatiles: (2 Chemical, 2 Utilities, 1 Steel, 1 Mining)

6 wastes x 1 lab x 2 (dup) = 12
6 spikes

TABLE 18 - Test Series 3: TCLP vs EP TOX

- o 15 wastes
- o each waste tested in two (2) labs
- o EP Tox run on each waste*
- o Each test run in duplicate
- o Inorganics only

15 wastes x 2 labs x 2 (dup) = 60 samples
15 spikes x 2 labs x four (4) metals

***TCLP results available from Series 2**

TABLE 19 - Test Series 4: Acetate Medium vs DI Water

- o 6 wastes (3 for metals only, one for volatiles only, one for semi-volatiles only, and one for volatiles plus semi-volatiles.)
- o each waste tested in one (1) lab
- o TCLP run with DI water*
- o Each test run in duplicate

Inorganics: (1 Steel, 1 Mining, 1 Lead)
3 wastes x 1 lab x 2 (dup) = 6 samples
1 spike/waste for four (4) metals

Volatiles: (1 Chemical, 1 Textile)
2 wastes x 1 lab = 2 samples
screening information available from Test Series 1 or 2
analysis: 2 x 2 (dup)
spikes: 2

Semi-Volatiles: (1 Chemical, 1 Utilities)
2 wastes x 1 lab x 2 (dup) = 4
2 spikes

*Acetate buffer data available from Test Series 1 or 2.

For all tests, "total method spikes" were employed. The spiking solutions used were prepared as described in Tables 20 and 21. The objectives in using these spikes were:

(1) to develop comparative data on EP and TCLP "recovery" for inorganics, recognizing that absolute values for spike recovery would not necessarily be significant due to potential interaction with the waste.

(2) to observe recovery of volatile organics through the ZHE procedure.

(3) to provide semi-volatile data of some value, since it was suspected that very few, if any semi-volatile organics would be present in the wastes to be tested.

2.2.3 Reporting of Results

Laboratories were asked to complete all applicable portions of Phase II data sheets shown in Appendix D. QA data were not reported but were to be retained by the laboratories.

TABLE 20 - PREPARATION OF SPIKING SOLUTIONS - ORGANICS

Solution A

	Preparation	Concentration* ug/ml
1,1-Dichloroethylene	50 ul @ 10,000 ug/ml	25
Trichloroethylene	50 ul @ 10,000 ug/ml	25
Chlorobenzene	50 ul @ 10,000 ug/ml	25
Toluene	50 ul @ 10,000 ug/ml	25
Benzene	50 ul @ 10,000 ug/ml	25

Final Volume = 20.0 ml Absolute Methanol

Solution B

	Preparation	Concentration* ug/ml
Pentachlorophenol	2.00 ml @ 10,000 ug/ml	400
Phenol	2.00 ml @ 10,000 ug/ml	400
2-Chlorophenol	2.00 ml @ 10,000 ug/ml	400
4-Chloro-3-methylphenol	2.00 ml @ 10,000 ug/ml	400
4-Nitrophenol	2.00 ml @ 10,000 ug/ml	400
1,2,4-Trichlorobenzene	1.00 ml @ 10,000 ug/ml	200
Acenaphthene	1.00 ml @ 10,000 ug/ml	200
2,4-Dinitrotoluene	1.00 ml @ 10,000 ug/ml	200
Pyrene	1.00 ml @ 10,000 ug/ml	200
N-Nitroso-di-N-propylamine	1.00 ml @ 10,000 ug/ml	200
1,4-Dichlorobenzene	1.00 ml @ 10,000 ug/ml	200

Final Volume = 50 ml Absolute Methanol

Solution C

	Preparation	Concentration* ug/ml
Pentachlorophenol	2.00 ml @ 10,000 ug/ml	800
Phenol	2.00 ml @ 10,000 ug/ml	800
2-Chlorophenol	2.00 ml @ 10,000 ug/ml	800
4-Chloro-3-methylphenol	2.00 ml @ 10,000 ug/ml	800
4-Nitrophenol	2.00 ml @ 10,000 ug/ml	800
1,2,4-Trichlorobenzene	1.00 ml @ 10,000 ug/ml	400
Acenaphthene	1.00 ml @ 10,000 ug/ml	400
2,4-Dinitrotoluene	1.00 ml @ 10,000 ug/ml	400
Pyrene	1.00 ml @ 10,000 ug/ml	400
N-Nitroso-di-N-propylamine	1.00 ml @ 10,000 ug/ml	400
1,4-Dichlorobenzene	1.00 ml @ 10,000 ug/ml	400

Final Volume = 25 ml Absolute Methylene Chloride

*Confirmed to within 10% by GC/MS analysis

TABLE 21 - PREPARATION OF SPIKING SOLUTION D - INORGANICS

Preparation:

15.39 g $Cr(NO_3)_3.9H_2O$
3.19 g $Pb(NO_3)_2$
3.26 g $CdCl_2$
17.70 g $BaCl_2.2H_2O$
→ 1.00 liter deionized water

Analysis after 2 weeks of storage:

Ba: 9.8 g/l
Cd: 2.0 g/l
Cr: 2.0 g/l
Pb: 2.1 g/l

3.0 DATA EVALUATION

3.1 Phase IA

The testing in this first phase was designed to familiarize the laboratories with the procedure and develop some preliminary data. Therefore, the discussion of these data will be brief.

Only one of the five industry wastes tested in Phase IA was found to be "hazardous" by toxicity characteristic (Waste #4 - high lead values in both EP and TCLP leachates). One other waste from the group is a borderline case. For Waste #3, one high EP lead concentration was recorded in a set of two replicates (<0.125; 9.7 mg/L) The two TCLP values for the same sample, in the same laboratory, were recorded as <0.125 mg/L. The protocol required analysis by the method of known additions. Assuming this was followed, simple analytical error is not likely, although always possible. Two potential explanations of the high lead values are (1) sample variability and (2) sample contamination in the laboratory. It should be noted that for these five wastes and waste #6, the variability of determined values for lead is higher than for any other parameter. These data and subjective information on the samples suggest that particulate lead in non-homogeneous samples is the likely cause of this variability. Such spurious results from sampling non-homogeneous materials <u>are</u> representative of real world situations. These data point up the major influence of sampling and sub-sampling on test results.

Data collected on Wastes #1 through #5 were not intended for statistical evaluation. As can be seen from the compilation of data to which this report is an addendum, visual comparison of duplicate values and of TCLP with EP results shows no major trends. As would be expected, there is better agreement between duplicate values using the same procedures than between values generated from the two different procedures.

Waste #6 was "split" with considerable care and attention, as described in Section 2.1.1, and distributed to all six participating laboratories. Table 22 summarizes data on Waste #6 and presents the estimated precision as described by the relative standard deviation (RSD). Both the TCLP and EP means and RSDs are compared. RSDs range from 32.3% (EP-Cd) to 161% (EP-Pb).

For this waste, no trend is found in EP vs TCLP precision across all parameters. For arsenic, chromium, and lead, the precision of the TCLP was better than that of the EP Toxicity test, whereas for barium and cadmium, the EP Toxicity precision was better than that of the TCLP. Mercury and selenium were undetected. Similarly, no significant trend is obvious from a comparison of means. A t-test shows that only in the case of barium was there a significant difference between the EP and TCLP means, at the 95% confidence level. Comparison of the relative standard deviations calculated for the EP and TCLP on this waste with published analytical method precision data shows an expectable difference in all but one case. For cadmium, the RSDs for both the EP and TCLP are very close to that of the analytical method (32.3% and 39.6% vs 30%).

TABLE 21 STATISTICAL EVALUATION: WASTE #6

All Units = mg/L except as noted

	Arsenic	Barium	Cadmium	Chromium	Lead	Phenols	TOX
$\bar{x}$ EP	0.048	5.9	0.19	0.090	293	-	-
$\bar{x}$ TCLP	0.039	14.5	0.17	0.069	256	0.825	2.99
s_{EP}	0.024	3.77	0.061	0.065	471	-	-
s_{TCLP}	0.021	10.5	0.067	0.048	241	0.415	2.85
t of means (95%)	0.928	2.95	0.761	0.68	0.254	-	-
df	20	22	22	12	22	12	11
Significant	No	Yes	No	No	No	-	-
% RSD EP	50.4	63.8	32.3	72.2	161	-	-
% RSD TCLP	43.8	72.4	39.6	69.0	94	50.3	95.3
Published % RSD[1]	2.2	3.7	30	37.6	34.9	1.1	5.4
Target Value[2]	0.050	5.0	0.071	0.093	0.367	0.447	0.100
EPA Method #	206.2	208.1	213.1	218.1	239.1	420.2	SW846(9020)

- not applicable

$$t = \frac{|\bar{x} - \bar{y}|}{s_{avg}} \sqrt{\frac{n\,m}{n+m}}$$

where: $\bar{x}$ = mean of EP data
n = total # of EP values
s_1 = standard deviation of EP values
$\bar{y}$ = mean of TCLP data
m = total # of TCLP values
s_2 = standard deviation of TCLP values

$$df = (n + m - 2)$$

$$s_{avg} = \frac{(s_1 n)\ (s_2 m)}{n + m}$$

Note 1: All published RSDs were obtained from EPA-600/4-79-020, March, 1979, Methods for Chemical Analysis of Water and Wastes except that for TOX which was determined in house at Lancy Laboratories based on twenty (20) replicate TOX determinations on a 0.100 mg/L standard in deionized water over a 2-month period.

Note 2: Concentration of solutions utilized for determination of published RSDs referenced in Note 1 above.

Precision data on the organic parameters measured in Phase IA are similar to those on the inorganic parameters. Since these parameters (phenols by colorimetry and TOX) are merely surrogates, as explained in Section 2, no further attempt will be made to elaborate on the potential significance of these data.

In general, there was no case in Phase IA in which a waste was found to be "hazardous" by one leaching procedure and not by the other. The range of values produced by the application of ±3 standard deviations to the means obtained for Waste #6, however, indicates that neither the EP nor the TCLP are sufficiently precise to allow reliance on one determination. For example, for chromium with means of 0.09 mg/l (EP) and 0.069 mg/l (TCLP), the application of the 99% confidence interval (±3 SDs) yields ranges of 0 - 0.285 mg/l (EP) and 0 - 0.213 mg/l (TCLP). Since these values are all below regulatory limits, the uncertainty in the true value is not significant. However, if the mean had been nearer the regulatory limit, for example 3 mg/l, and a similar RSD were applicable, the range of uncertainty would extend beyond the regulatory level. And, by the same process, a result of 5 mg/l, the level classifying a waste as hazardous, exists in a range extending well above and below the regulatory limit (at ±3 RSDs, using 70% RSD, the value 5 exists in a range 0 - 15.5 mg/l). It is clear from these data that neither the EP nor the TCLP provide results which are dependable for decision-making based on the analysis of one sample.

3.2 Phase II Precision Study Data

Six wastes were used in the precision study test series, one from each sponsoring organization. All tests were run in duplicate and a "spike" was run with each set in each of the laboratories. The overall precision of the TCLP was evaluated by calculating the relative standard deviation. Intra- and inter-laboratory precision were compared using percent relative difference calculations.

3.2.1 Inorganics

Intra- and inter-laboratory TCLP precision data for inorganics are given in Table 23. Only those data sets which contained no "less than" values were used for calculation of standard deviations. Since the majority of data points reported were "less than" values, the quantity of data available to estimate the precision of the TCLP is considerably less than would be indicated by the number of analyses performed. All calculations are based on the data previously submitted August 12 to Docket #F-86-TC-FFFFF.

The TCLP RSDs range from 7.4% (surprisingly, for lead) to 63%. No correlation between standard deviation and parameter was found. For example, RSDs for barium ranged from 8.7% to 56%.

TABLE 23 - COMPARISON OF INTRA- AND INTER-LABORATORY PRECISION

TCLP - INORGANICS

Waste #	Parameter	Mean Concentration mg/l in leachate	SD	%RSD	Intra-lab[1] Average % RD[3]	Inter-lab[2] Average % RD[3]
201	Ba	0.62	0.304	49	25	74
204	Ba	0.40	0.224	56	34	85
	Cr	3.3	1.68	51	35	64
205	Ba	2.3	0.201	8.7	4.7	12
208	Ba	1.2	0.264	22	2.4	31
	Cd	0.057	0.010	18	1.3	25
	Pb	0.70	0.081	12	6.4	16
212	As	0.022	0.0099	45	4.8	56
	Cd	1.5	0.235	16	4.0	22
	Cr	0.31	0.061	20	13	28
	Pb	23	10.9	47	16	71
	Se	0.12	0.075	63	26	80
214	Cd	0.098	0.014	14	6.0	20
	Pb	49	3.6	7.4	10	4.5

[1]Intra-laboratory Percent Relative Difference (Intra-lab % RD) = $\frac{\frac{|R_1 - R_2|}{R_1 + R_2}}{2} \times 100$

Where R_1 and R_2 = replicate values from one laboratory

[2]Inter-laboratory Percent Relative Difference (Inter-lab % RSD) =

$$\frac{\frac{|M_1 - M_2|}{M_1 + M_2} + \frac{|M_1 - M_3|}{M_1 + M_3} + \frac{|M_2 - M_3|}{M_2 + M_3}}{3} \times 100$$

Where M_1, M_2 and M_3 = mean values from three laboratories

[3]Average Percent Relative Difference (Avg % RD) = $\frac{\Sigma \text{ \% RD}}{n}$ n = number of values

A comparison of intra- and inter-laboratory precision is desirable since logic and experience indicate a substantial difference exists between repeatability within one laboratory and reproducibility among laboratories. The data in Table 23 confirm this assumption, showing significantly larger differences between values obtained in different laboratories than between those obtained in the same laboratory. Figures 1 and 2 present these data graphically, using average values. Percent relative difference is used for this comparison, since the quantity of data is limited (only duplicate values are available for intra-laboratory precision estimation). A visual comparison of the magnitude of the % RSD values and the Inter-lab Average % RD values allows some evaluation of the relationship between standard deviation and relative difference for these data. (The Inter-laboratory Average % RD values are 24-52% higher than the respective % RSD values.) This also allows some evaluation of the Intra-lab Average % RD values relative to overall standard deviation values.

In only one case, (the lead determination on Waste #214) does the intra-lab value exceed the inter-lab value, but this occurs in a situation where all reported values are within ±20% of the mean.

A relationship between precision and concentration of analyte does not appear to exist in these data. RSDs of greater than 40% are recorded for levels below 1 mg/l as well as for levels above 20 mg/l; low RSDs (<15%) are recorded for these same levels.

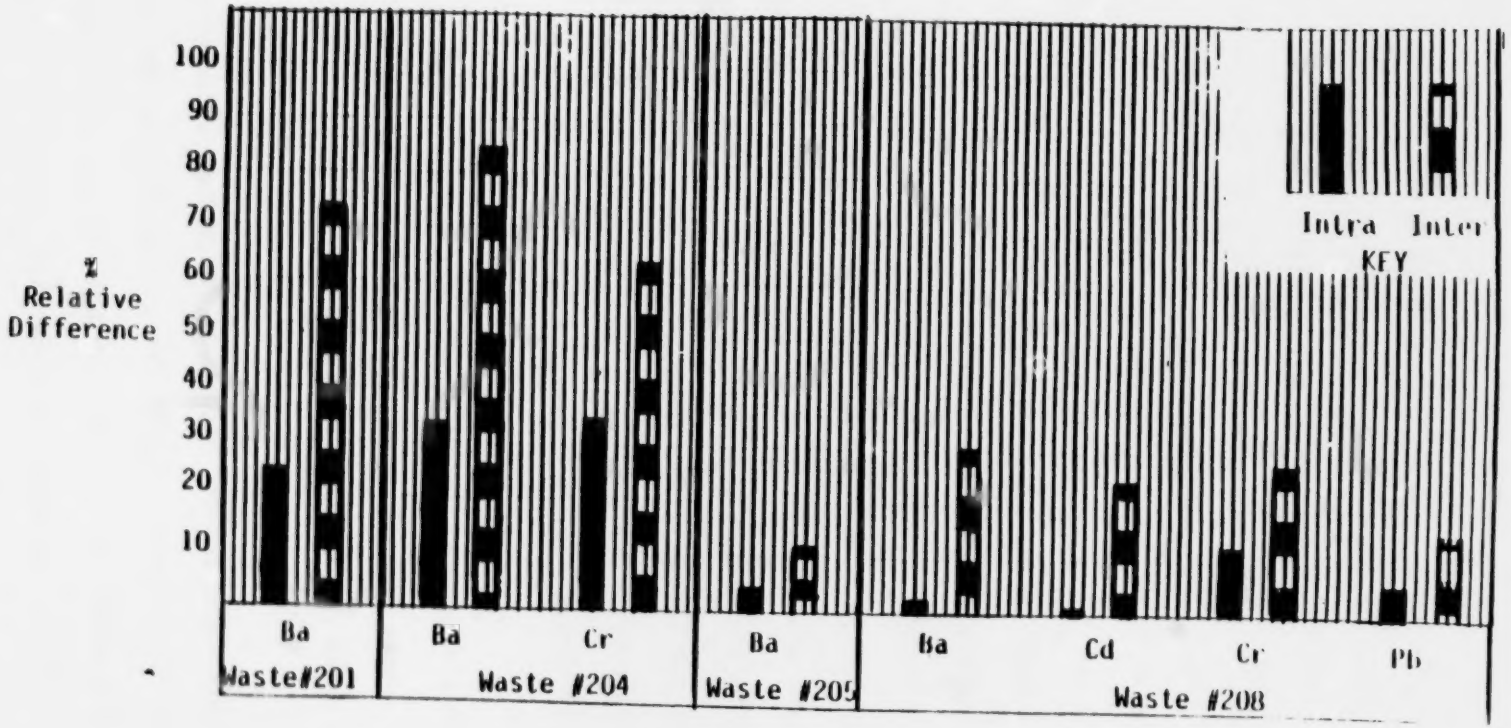

FIGURE 1 INTRA- vs INTER-LABORATORY PRECISION - TCLP

WASTES #201, 204, 205, and 208 - Inorganics

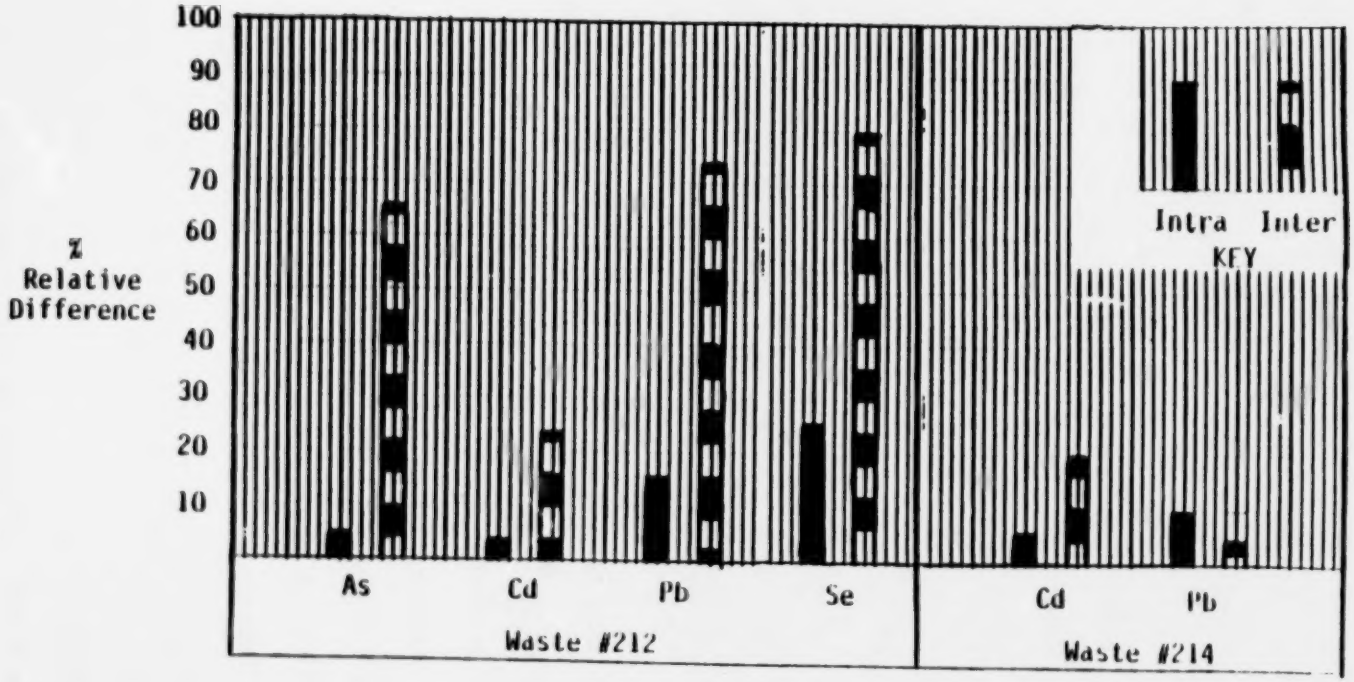

FIGURE 2 INTRA- vs INTER-LABORATORY PRECISION - TCLP

WASTES 212 and 214

There does appear to be a relationship between waste type and precision. However, this is based on a small sampling and may not be valid for a larger universe of wastes. In this study, some general consistency was found for RSDs within a waste type. For example:

Waste #204 - RSDs >50<60 (2 values)

Waste #208 - RSDs >12<22 (3 values)

Waste #214 - RSDs >7<14 (2 values)

Although these figures indicate some correlation, the data on Waste #212 do not fit the pattern, as can be seen in Table 21. Again, logic and experience indicate that precision of a procedure such as the TCLP would be influenced by sample type more than by any other factor.

These data do include one value which is sufficiently close to the regulatory level to warrant scrutiny. The mean chromium value on Waste #204 is given as 3.3 mg/l. The regulatory level is 5 mg/l. However, the standard deviation found is 1.68 mg/l, and ± 3 SDs gives a range of 0 - 8.3 mg/l. The range of actual recorded values is 0.99 - 5.3 mg/l. Interpretation of these data relative to the classification of the waste as "hazardous" is particularly problematic. (See also Section 3.4)

3.2.2 Organics

Of the three wastes tested for volatiles in the precision study, only one waste, #208, provided sufficient data on which to base a

standard deviation. The others had only "less than" data (plus one set of only two values reported for methylene chloride: 0.001, 0.005 mg/l). Intra- and inter-laboratory precision for Waste #208 are provided in Table 24. The relative standard deviations for the four volatile organics found are comparable to those for the inorganic parameters discussed above. As in the case of the inorganic parameters, the inter-laboratory % RD is considerably higher than the intra-laboratory % RD. This difference is much greater for volatile organics than for inorganics. For organics, the intra- vs inter-laboratory % RD Δ is 60% (range of 20 - 23%), whereas for inorganics, this Δ is 31% (range of 7.3 - 55%). See Figure 3. All of the values reported for this waste fall well above the proposed regulatory level; therefore, evaluation of the effect of the standard deviations found on hazardous classification is not possible for these data. However, at or near regulatory levels, standard deviations of 24 to 78% would provide a wide range of uncertainty (up to a factor of 2.3.) For trichloroethylene, for example, a measured value of 0.08 mg/l, while above the proposed regulatory level of 0.07 mg/l, would fall within a range of uncertainty of 0-0.18 mg/l if the RSD obtained in this study is representative. In general, however, the standard deviations obtained for this sample are better than anticipated, particularly considering the nature of the ZHE and the procedural problems reported (see Appendix F).

The two samples tested for semi-volatiles in the precision study were not a source of data. Neither sample contained semi-volatiles at concentrations above the detection limits.

TABLE 24 - COMPARISON OF INTRA- AND INTER-LABORATORY PRECISION

TCLP - Organics

Waste#	Parameter	Mean Concentration mg/l in leachate	SD	%RSD	Intra-lab[1] Average % RD[3]	Inter-lab[2] Average % RD
208	1,1,1,2 Tetra-chloroethane	390	217	56	6.6	72
	1,1,2,2-Tetra-chloroethane	670	185	28	8.9	20
	1,1,2-Trichloro-ethane	36	8.82	24	14	26
	Trichloroethylene	73	57.2	78	21	123

[1]Intra-laboratory Percent Relative Difference (Intra-lab % RD) = $\frac{|R_1 - R_2|}{\frac{R_1 + R_2}{2}} \times 100$

Where R_1 and R_2 = replicate values from one laboratory

[2]Inter-laboratory Percent Relative Difference (Inter-lab % RSD) =

$$\frac{\frac{|M_1 - M_2|}{\frac{M_1 + M_2}{2}} + \frac{|M_1 - M_3|}{\frac{M_1 + M_3}{2}} + \frac{|M_2 - M_3|}{\frac{M_2 + M_3}{2}}}{3} \times 100$$

Where M_1, M_2 and M_3 = mean values from three laboratories

[3]Average Percent Relative Difference (Avg % RD) = $\frac{\sum \%\ RD}{n}$ n = number of values

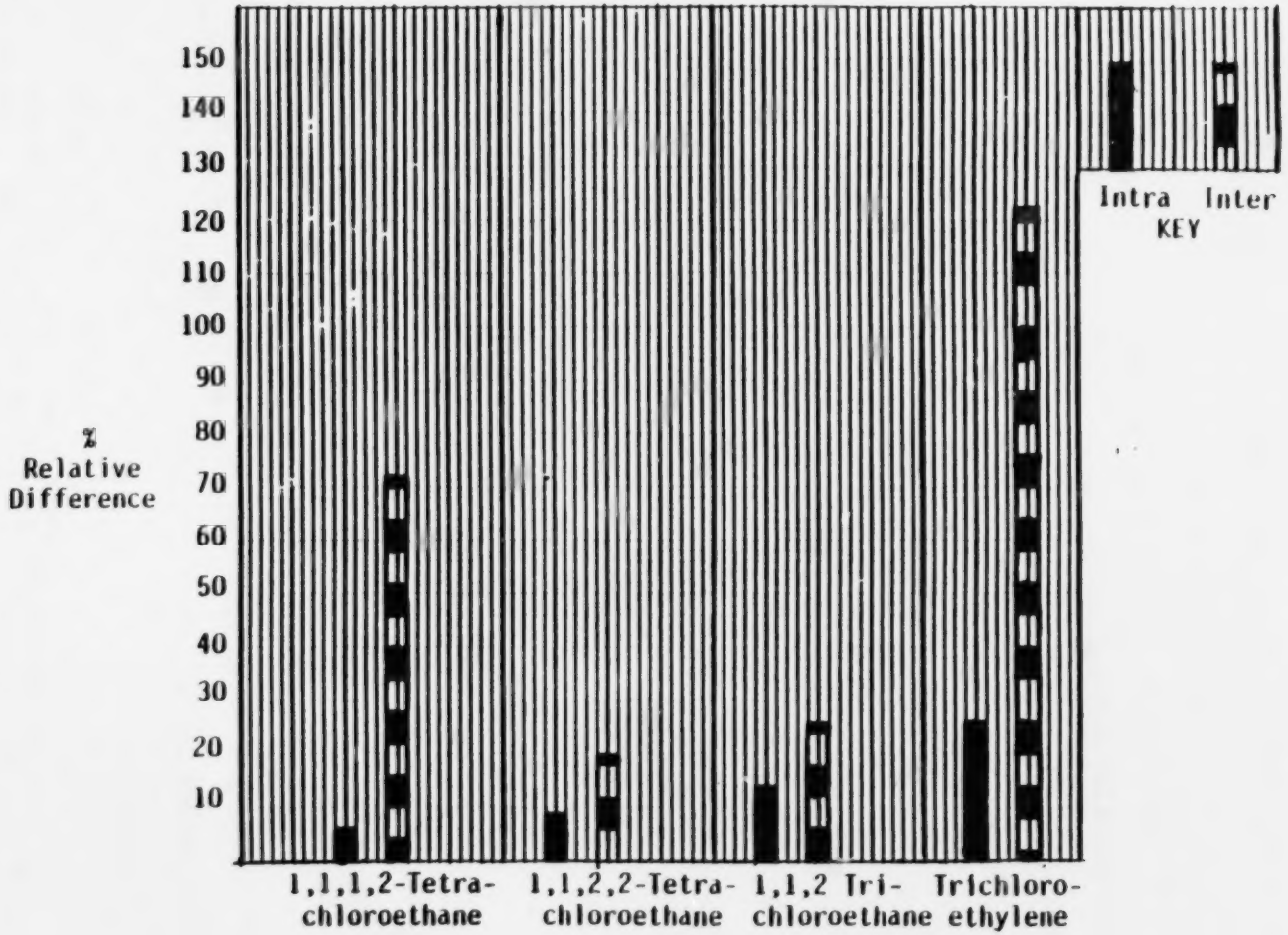

FIGURE 3 INTRA- vs INTER-LABORATORY PRECISION - TCLP

WASTE #208 - Organics

3.3 Phase II Waste Characterization Data

Of all the fifteen wastes tested, seven were identified as "hazardous" by the proposed criteria, seven were identified as "non-hazardous", and one waste (#204) was a borderline case. Waste #204 was identified as "hazardous" by one laboratory's TCLP chromium results. This waste was part of the precision study and was tested in three laboratories. The other two sets of TCLP chromium data were below the proposed regulatory level. These data are repeated here because of their significance.

	Lab #1	Lab #2	Lab #3	
Cr	5.3	0.99	2.70	
	5.2	2.83	2.58	All units mg/l

The mean value for this set of data is 3.3 mg/l. The regulatory level for determination of hazardous or non-hazardous classification is 5 mg/l. The EP Toxicity data for chromium on this sample were considerably lower.

	Lab #1	Lab #2	
Cr	0.040	0.970	
	0.050	0.790	All units mg/l

In this particular case, the waste evaluated by EP Toxicity would have been judged to be "non-hazardous", whereas when evaluated by the TCLP procedure, the waste would have been judged to be "hazardous" by one laboratory's results. (See Also Section 3.4)

The following paragraphs describe particular features observed for individual wastes tested.

Waste #201

Most inorganic parameters were either not present or present in very low concentrations. This waste was tested for volatiles which were either not detected or present in very low concentrations, far below the regulatory levels.

Waste #202

No inorganic parameters were found in any significant concentration. Volatile organics, however, were detected in the TCLP leachate (ZHE). One of those compounds detected was reported at a level above the proposed regulatory level (trichloroethylene - 0.24 mg/l). However, this same compound was reported as not detected in the replicate determination, and the laboratory reported suspect values due to high blanks. Note that none of these compounds were found in the screening procedure. This points out the need for frequent blanks and the difficulty in maintaining low blanks in the ZHE (See Section 3.7).

Waste #203

No inorganics of significance were found, but volatile organics were detected, some at levels above regulatory levels. These data are also reported as suspect due to high blanks.

Waste #205

No inorganics of significance were found. This waste was tested for semi-volatiles, but none were detected.

Waste #206

All inorganics with the exception of mercury and lead were detected in the TCLP leachate, but all were present at levels well below the regulatory levels. Semi-volatiles data were incomplete at the time of this report.

Waste #207

Only selenium, arsenic, and barium were detected in TCLP leachate. The levels found were well below regulatory levels. This waste was also tested for semi-volatiles, but none were detected.

Waste #208

All inorganics with the exception of arsenic were detected at low levels in the TCLP leachates. Volatiles were detected at levels far exceeding regulatory levels. A total of ten volatile organic compounds were detected in the TCLP leachate. Two semi-volatiles were also detected. Based on the data collected in this study, this waste would be classified as "hazardous" under the proposed regulation.

Waste #209

All inorganics with the exception of arsenic, mercury, and selenium were found in the TCLP leachate. For the most part, values were low, but lead values were greater than 1 mg/l, approaching the regulatory limit of 5. This waste was also tested for volatiles and semi-volatiles and found to be "hazardous" under the proposed regulation. This waste was identified by the originator as the same type of waste as #208. Although the data produced were not identical, there were many similarities between the two sets of data. In both cases, the wastes would be classified as "hazardous". Minor differences in concentration levels, although of interest from an academic standpoint, are not significant since the contribution of sampling variables is unknown.

Waste #210

No inorganic components were found in significant concentrations. No other tests were conducted.

Waste #211

This waste was found to be hazardous by virture of the high lead concentration in the TCLP leachate (33 mg/l). All other inorganic components with the exception of arsenic were present in the TCLP leachate at low to moderate concentrations, below regulatory levels.

Waste #212

A classification of "hazardous" would result from these data, based on high lead and cadmium values in the TCLP leachate. This waste was tested in three laboratories. The lead values varied considerably, but all were above the regulatory level of 5 mg/l. All other inorganic components were present at low levels. As would be expected from the more aggressive chemical behavior of acetate toward lead, the TCLP performed with DI water produced lead levels in the leachate well below those obtained with the acetate extraction fluid called for in the protocol and well below regulatory levels.

Waste #213

Only arsenic, barium, cadmium, and lead were found in the TCLP leachate. These components were present at low concentrations, below the regulatory levels.

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Waste #214

Lead values in the TCLP leachate would classify this waste as "hazardous". All other inorganic parameters were detected but at low levels, well below the regulatory levels. Tests for semi-volatiles detected only one compound, pentachlorophenol, at a very low concentration (0.003 mg/l). This value is so near the detection limit that no significance is placed on it.

Waste #215

No inorganic components were detected at significant levels. This waste was also tested for semi-volatiles. As with Waste #214, pentachlorophenol was detected at 0.004 mg/l, but was not considered significant.

3.4 Comparison of TCLP and EP Results

Data on all 15 wastes are presented in Table 25, comparing TCLP and EP Toxicity results. In those cases where sufficient data points were available (precision study samples, excluding "less than" values) relative standard deviations were calculated, and a t-test was used to evaluate the standard deviations of the two procedures. As can be seen from these data, the t-test shows a significant difference between the two procedures in six of eleven cases. As discussed above, very little correlation can be found between precision and various factors such as analyte, concentration level, etc.. An examination of the mean values, however, shows that, with the exception of 5 cases out of 105, the TCLP values are higher than the respective EP values.

The standard deviations calculated for the EP data range from 6.6% RSD to 101% RSD. This is a somewhat wider range than found for the TCLP. Although both procedures exhibited a precision much lower than desirable, in these data only one instance was found in which a waste might have been classified as "hazardous" by the TCLP procedure and "non-hazardous" by the EP procedure (Waste #204).

TABLE 25 COMPARISON OF TCLP AND EP TOXICITY DATA

Waste#	Parameter	Mean TCLP	Mean EP	TCLP % RSD	EP %RSD	t value	Critical t at 95%
201	As	<0.2	<0.2				
	Ba	0.62	0.15	49	93	3.1	2.3
	Cd	<0.02	<0.02				
	Cr	<0.05	<0.05				
	Pb	<0.1	<0.1				
	Hg	<0.0005	<0.0002				
	Se	<0.2	<0.2				
202	As	<0.001	0.001				
	Ba	<0.1	<0.1				
	Cd	0.01	<0.01				
	Cr	<0.01	0.01				
	Pb	0.06	<0.01				
	Hg	<0.0003	0.0006				
	Se	<0.001	<0.001				
203	As	<0.008	<0.01				
	Ba	2.0	<0.04				
	Cd	<0.008	<0.01				
	Cr	<0.01	<0.04				
	Pb	<0.04	<0.20				
	Hg	<0.001	<0.0003				
	Se	0.014	<0.01				
204	As	<0.2	<0.04				
	Ba	0.40	0.31	56	16	0.88	2.3
	Cd	<0.02	<0.02				
	Cr	3.3	0.46	51	106	3.59	2.3
	Pb	<0.061	<0.061				
	Hg	<0.0005	<0.0005				
	Se	<0.2	<0.05				

TABLE 25 CONTINUED

Waste#	Parameter	Mean TCLP	Mean EP	TCLP % RSD	EP % RSD	t Value	Critical t at 95%
205	As	<0.2	<0.2				
	Ba	2.3	0.70	8.7	17	15	2.3
	Cd	<0.015	<0.02				
	Cr	<0.020	<0.012				
	Pb	<0.1	<0.1				
	Hg	<0.0005	<0.0005				
	Se	<0.2	<0.2				
206	As	0.007	<0.003				
	Ba	0.24	<0.15				
	Cd	0.021	0.016		73		
	Cr	0.077	<0.040				
	Pb	<0.001	<0.25				
	Hg	<0.0002	<0.0006				
	Se	0.052	0.034		39		
207	As	<0.012	<0.010				
	Ba	0.98	0.83		7.1		
	Cd	<0.002	<0.004				
	Cr	<0.012	<0.012				
	Pb	<0.061	<0.061				
	Hg	<0.0005	<0.001				
	Se	0.110	<0.04				
208	As	<0.010	<0.010				
	Ba	1.2	<0.60	22			
	Cd	0.057	0.051	18	33	0.81	2.3
	Cr	<0.060	<0.060				
	Pb	0.70	<0.15	12			
	Hg	<0.002	<0.0004				
	Se	<0.015	<0.010				
209	As	<0.010	0.011				
	Ba	1.6	0.29				
	Cd	0.16	0.057				
	Cr	0.080	<0.012				
	Pb	1.1	0.18				
	Hg	<0.0003	<0.0005				
	Se	<0.010	0.014				

TABLE 25 CONTINUED

Waste#	Parameter	Mean TCLP	Mean EP	TCLP % RSD	EP % RSD	t Value	Critical t at 95%
210	As	<0.2	<0.2				
	Ba	0.59	0.49		19		
	Cd	<0.02	<0.02				
	Cr	<0.05	<0.05				
	Pb	<0.1	<0.1				
	Hg	<0.0002	0.0004		63		
	Se	<0.2	<0.2				
211	As	<0.001	0.014		101		
	Ba	0.6	0.48		30		
	Cd	0.04	<0.03				
	Cr	1.8	1.2		30		
	Pb	33	20		76		
	Hg	0.0008	<0.0014				
	Se	0.14	0.23		22		
212	As	0.022	<0.01	45			
	Ba	<0.1	<0.01				
	Cd	1.5	1.4	16	9.1	0.81	2.3
	Cr	0.31	0.13	20	33	5.3	2.3
	Pb	23	38	47	8.2	3.0	2.3
	Hg	<0.001	<0.001				
	Se	0.12	0.11	26	79	0.34	2.3
213	As	0.080	0.016				
	Ba	0.22	0.036				
	Cd	0.076	0.032				
	Cr	<0.04	<0.04				
	Pb	0.053	<0.05				
	Hg	<0.0003	<0.0003				
	Se	<0.01	<0.01				

TABLE 25 CONTINUED

Waste#	Parameter	Mean TCLP	Mean EP	TCLP % RSD	EP % RSD	t Value	Critical t at 95%
214	As	<0.01	<0.004				
	Ba	<0.42	<0.1				
	Cd	0.098	0.085	14	6.6	1.9	2.3
	Cr	<0.10	<0.07				
	Pb	49	34	7.4	30	4.4	2.3
	Hg	<0.001	<0.001				
	Se	<0.020	<0.008				
215	As	0.046	0.054		59		
	Ba	1.8	0.99		62		
	Cd	<0.008	<0.004				
	Cr	<0.01	<0.02				
	Pb	<0.05	0.014		91		
	Hg	<0.001	<0.001				
	Se	0.019	<0.008				

One major concern regarding the differences between the EP and the TCLP is the difference in filter media. It was postulated that the use of the glass fiber filter in the TCLP would result in higher concentrations of materials in the leachate. It is possible that the differences in TCLP and EP values reported above are related to this difference in filter media. No tests were specifically run to isolate the effect of the filter media, and therefore, no firm conclusion can be reached on this point.

Another factor expected to influence results is the difference in extraction fluids and the potential resulting difference in pH and buffer capacity of the leachates. Table 26 summarizes data on extraction fluids used and initial and final pHs reported by the laboratories. It can be seen that, in general, final pHs achieved in TCLP leachates were very similar to those achieved in EP leachates. As is indicated in the table, some laboratories reported initial TCLP pHs prior to addition of the extraction fluid while others gave pHs after the addition of extraction fluid. In those instances where the pHs are reported <u>after</u> the extraction fluid was added, it can be seen that pH may have influenced the leaching characteristics of the wastes in a different fashion in the TCLP than in the EP. The progressive addition of buffer solution, resulting in a gradual change in pH in the EP, is compared with a situation in the TCLP where the pH is either constant or in some cases lower initially than at the conclusion of the procedure. This effect would be significant for some wastes but not for others.

TABLE 26-COMPILED pH DATA, TCLP AND EP TOXICITY

Waste #	Lab #	Extraction Fluid	TCLP Data Initial pH Run #1	TCLP Data Final pH Run #1	TCLP Data Initial pH Run #2	TCLP Data Final pH Run #2	EP Data Initial pH Run #1	EP Data Final pH Run #1	EP Data Initial pH Run #2	EP Data Final pH Run #2
201	#1	#1	NR	NR	NR	NR	7.1	4.8	7.4	4.8
	#2	#1	4.93*	4.99	4.94*	5.04	--	--	--	--
	#3	#1	7.2	4.75	7.1	5.4	7.36	5.07	7.36	5.02
202	#4	#1	8.0	5.0	8.0	5.0	7.70	5.20	7.95	5.00
203	#5	#1	5.02*	5.03	5.03*	5.03	6.96	4.61	6.95	4.97
	#6	—	--	--	--	--	5.6	5.5	5.5	5.1
204	#1	#2	NR	NR	NR	NR	6.5	5.0	6.6	5.0
	#2	#2	3.43*	5.08	3.45*	5.08	7.18	4.80	7.20	4.83
	#3	#2	7.1	4.4	7.1	4.5	--	--	--	--
205	#1	#1	NR	NR	NR	NR	--	--	--	--
	#2	#1	4.88*	5.41	4.84*	5.37	8.37	4.92	8.62	4.89
	#3	#1	8.2	5.0	8.2	5.1	8.2	5.22	8.2	5.19
206	#1	#2	NR	NR	NR	NR	11.1	6.0	11.1	6.2
	#4	—	--	--	--	--	10.80	6.50	10.80	6.50
207	#1	#2	5.16	5.30	5.14*	5.34	9.02	4.87	8.87	5.02
	#5	--	--	--	--	--	9.09	4.94	9.15	5.03
208	#4	#1	6.0	5.5	6.0	5.0	6.65	5.10	6.40	5.15
	#5	#1	5.02*	5.11	5.00*	5.15	--	--	--	--
	#6	#1	5.0*	5.0	5.1*	5.1	5.7	5.9	6.0	6.1
209	#2	--	--	--	--	--	6.65	4.94	6.92	4.89
	#6	#1	5.2*	5.2	5.1*	5.1	--	--	--	--
210	#1	--	--	--	--	--	10.0	5.0	10.2	5.3
	#3	#2	10.2	6.9	10.2	6.9	10.6	6.46	10.62	6.56
211	#2	—	--	--	--	--	12.19	11.70	12.22	11.62
	#4	#2	11.7	12.0	11.7	12.0	12.20	11.80	12.05	11.80

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TABLE 26-CONTINUED

Waste #	Lab #	Extraction Fluid	TCLP Data Initial pH Run #1	TCLP Data Final pH Run #1	TCLP Data Initial pH Run #2	TCLP Data Final pH Run #2	EP Data Initial pH Run #1	EP Data Final pH Run #1	EP Data Initial pH Run #2	EP Data Final pH Run #2
212	#4	#2	9.9	5.0	9.9	5.0	--	--	--	--
	#5	#2	4.08*	4.62	4.09*	4.61	8.27	4.88	10.06	4.88
	#6	#2	4.4*	4.4	4.4*	4.4	5.0	5.1	5.1	5.1
213	#6	#1	5.0*	5.0	5.1*	5.1	5.3	5.4	5.6	5.6
214	#4	#1	6.9	5.0	6.9	5.0	8.10	5.20	8.20	5.15
	#5	#1	5.03*	5.54	5.01*	5.45	6.10	5.14	6.10	5.14
	#6	#1	5.2*	5.2	5.1*	5.2	--	--	--	--
215	#1	--	--	--	--	--	9.3	5.0	9.3	5.0
	#5	#1	5.02*	5.46	5.01*	5.45	9.07	5.20	9.21	5.19

*Measurement made after addition of extraction fluid.
NR=Not reported.

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Note that for Waste #204, a pH value of 3.4 is recorded as initial pH for one set of TCLP data. This would be likely to contribute to higher metal values in the leachate, such as the chromium values found for this waste in the TCLP. However, the laboratory reporting the low pH was not the same laboratory which found high chromium concentrations. The highest chromium value (5.3 mg/l) was reported by Laboratory #1, whereas the low initial pH was reported by Laboratory #2 (chromium values 0.99 and 2.83 mg/l). Unfortunately, Laboratory #1 did not report the leachate pH.

These data also show that some wastes were extracted at high pHs (Waste #206, #210, #211), even though the more agressive extraction fluid was used. Of these wastes, #211 was found to be "hazardous" in spite of the high pH leachate (lead at 33 mg/l), but the other two wastes were found to be "non-hazardous".

In general, there was good agreement between laboratories and within laboratories on pH values. Although there were a few exceptions (e.g. waste #204, #212), most pH values were at least within 0.5 pH units of one another within the same test procedure. Some greater differences occurred between EP and TCLP leachate pHs.

3.5 Comparison of DI Water and Acetate Medium

DI water results for inorganic parameters were obtained on only three samples (Waste #204, #212, and #215). Values obtained in the DI water leachate were lower than those obtained in acetate medium in most cases. This difference was most dramatic on Waste #212, for which the lead value in the TCLP leachate was 0.86 mg/l using DI water and ranged from 7.8 to 31.6 mg/l

using the standard acetate medium required in the TCLP. There were two cases in which higher values were obtained with DI water (0.39 mg/l selenium in DI water vs 0.05 to 0.26 mg/l in acetate medium and 0.34 mg/l arsenic in DI water vs 0.046 mg/l in acetate medium). In general, however, these data are in agreement with the large body of data in the literature indicating a much more agressive leaching of various materials by the acetate medium employed in the TCLP and EP than by deionized or distilled water.

TCLP tests with DI water were also performed on two samples for organics. Waste #201 was tested for volatiles with DI water, and none were detected. These results were comparable with those obtained with the standard acetate medium. Waste #209 was tested for semi-volatiles with DI water. The same compounds were found in the DI water extract as in the standard acetate extract at approximately the same levels. One parameter, hexachloroethylene, was detected at levels approximately 50% higher in DI water than in acetate (0.66 vs 0.42 mg/l).

3.6 "Spike Recovery"

As described in Section 2, "spikes" were added to all samples tested. One of the primary objectives was to evaluate comparative results between TCLP and EP procedures. Table 27 summarizes the spike recovery data for inorganic parameters. As can be seen, higher mean recoveries were obtained for all four parameters in the TCLP than in the EP. This is shown graphically in Figure 4. This phenomenon may be related to the fact, discussed earlier, that TCLP results were generally higher than EP results. Because

TABLE 27 COMPARISON OF SPIKE RECOVERIES
TCLP vs EP TOXICITY

	Barium		Cadmium		Chromium		Lead	
	TCLP	EP	TCLP	EP	TCLP	EP	TCLP	EP
Mean % Recovery	33	11	71	41	36	15	15	1.5
Range of Values, %	0-124	0-46	0-184	0-117	0-115	0-225	0-93	0-12
% RSD	94	118	73	91	88	373	165	208
t Value	347		232		166		286	
Critical t (95%)	2.1		2.1		2.1		2.1	

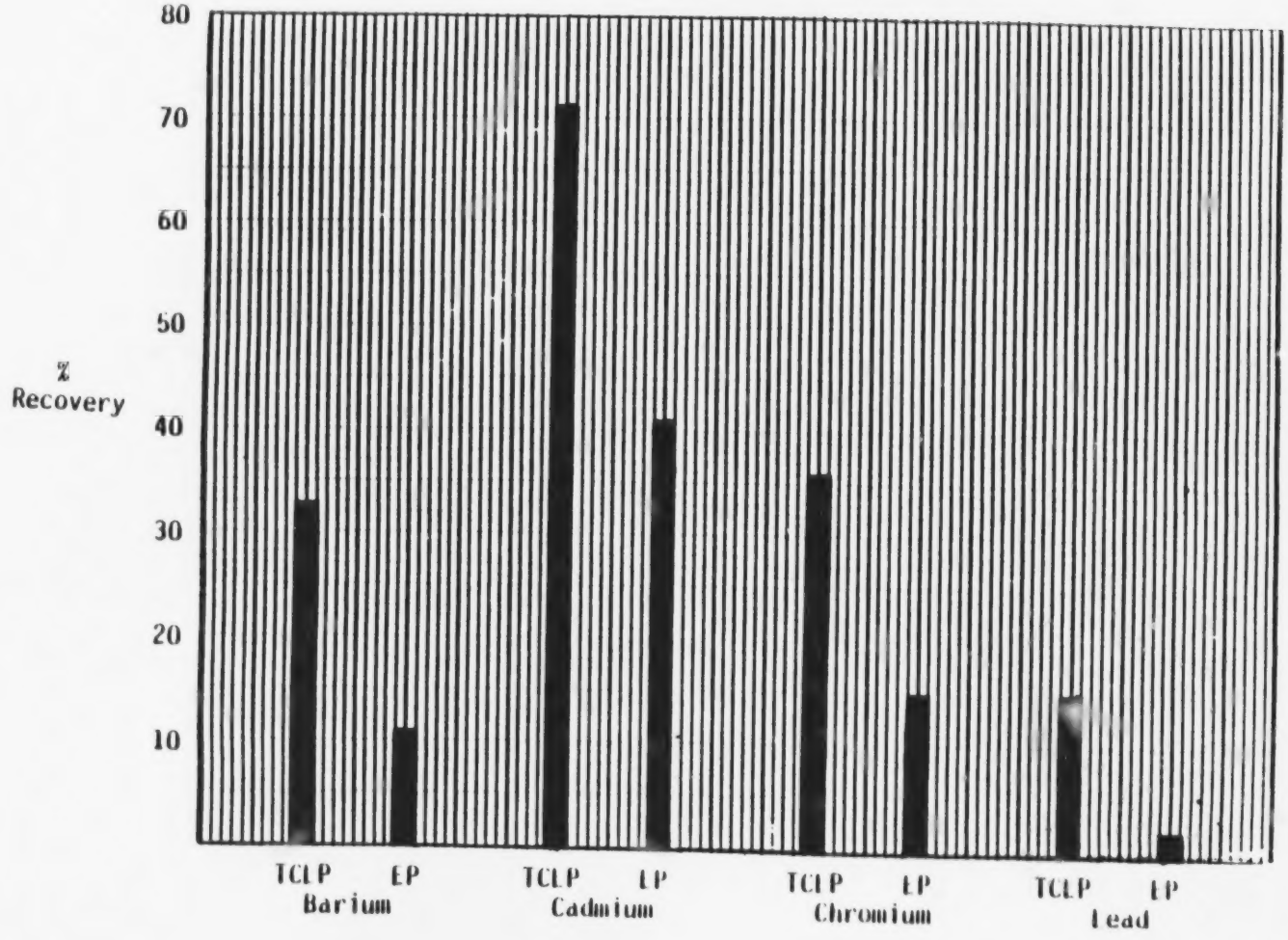

FIGURE 4 AVERAGE SPIKE RECOVERY

of the potential for interaction of spike parameters with components of each waste, it is difficult to interpret spike recovery values on an absolute basis. The difference between average spike recoveries for the TCLP and EP, however, is significant and implies that the TCLP is a more agressive leaching procedure than the EP.

For volatile organics, spike recovery was better than anticipated (See Table 28). Numerous problems with the ZHE device indicated that the spike recoveries would be poor. Although many results were indeed much lower than theoretical, several spike recoveries were better than 75%. As in the case of precision, the ability to recovery spikes seems to be related more to the nature of the waste than to any other factor.

TABLE 28 - TCLP SPIKE RECOVERIES - VOLATILE ORGANICS

Parameter	Mean % Recovery	Range of Values %	% RSD
Benzene	68	11-112	57
Chlorobenzene	45	3.5-78	64
1,1-Dichloroethylene	48	14-225	250
Toluene	45	7.4-85	72
Trichloroethylene	38	4-62	71

Recovery of semi-volatiles was less efficient, as can be seen in Table 29. In the majority of cases the semi-volatile spikes at theoretical values of 0.1 to 0.8 mg/l were not detected. In those cases where the compounds were detected, recovery averaged well below 50%.

TABLE 29 - TCLP SPIKE RECOVERIES - SEMI-VOLATILE ORGANICS

Parameter	Mean % Recovery	Range of Values %	% RSD
Pentachlorophenol	7.2	0-45	220
Phenol	14	0-38	110
1,4-Dichlorobenzene	11	0-36	140
2,4-Dinitrotoumcwi	25	0-114	170

A closer examination of the subject of spike recovery would be required to reach any substantial conclusions. Additional data are needed on the matrix components of the wastes tested to more thoroughly evaluate the potential interaction of the inorganic parameters with the wastes. Too few data are available on recovery of organics to warrant generalizations. Even though the data collected in this study are incomplete, they do add to the volume of knowledge on recovery of components from wastes through the TCLP leaching process.

3.7 TCLP Procedure Comments and Observations

Comments from participating laboratories on the mechanics of the TCLP are presented in Tables 30 and 31 and in Appendix F. In general, technicians find the TCLP procedure to be at least as managerable as the EP, with the exception of the ZHE. Many problems have been encountered in the operation of the ZHE devices. In addition, carryover from heavily contaminated samples is a major problem, since cleaning the devices is very difficult. Many of the problems associated with the ZHE will result in increased cost of testing due to both equipment costs (need for multiple devices) and technician time (labor-intensive procedure).

TABLE 30 - WASTE-SPECIFIC LABORATORY COMMENTS AND OBSERVATIONS

Waste #201: Lab #1 - No problems encountered with this sample for the EP and TCLP without ZHE. Bubbles exited the ZHE into the syringe when you filtered the samples for volatiles.

Waste #203: Lab #6 - The extraction fluid-waste slurries were extremely difficult to filter. The waste appeared to be filterable, but no initial liquid could be collected.

Waste #204: Lab #1 - Sample was very oily and tended to clog filters - both membrane and glass fiber. Extracts would not settle before filtration. Extraction vessels were very difficult to clean following the extractions, especially the ZHE. The top o-ring (barrel scrapper) tended to collect the residue in the folds. During filtration of the ZHE samples, bubbles appeared in the syringe from the ZHE. Sand particles were stuck in the metal screens on the Millipore ZHE.

Waste #210: Lab #1 - Representative sample was difficult to obtain due to large range of particle sizes. Cone and quarter method used to obtain sample size.

Waste #212: Lab #6 - Waste appeared to be filterable, but no initial liquid could be collected.

Waste #213: Lab #6 - Waste appeared to be filterable, but no initial liquid could be collected.

Waste #215: Lab #1 - Sample received was multi-phasic. It was very difficult to thoroughly mix the two layers. A thick brown sludge was obtained that did not release liquid during initial filtration.

TABLE 31 - LABORATORY COMMENTS AND OBSERVATIONS: ZHE

Laboratory #2

Some of the problems that were encountered with the ZHE are listed below:

-pitting of the ZHE with the possible loss of pressure
-loss of volatiles during the loading procedures for the ZHE
-some of the pistons required up to 50 psi to just move; however, after repeated usage, the piston moved more easily
-waste 201 did not prefilter well. Some of the sample was prefiltered in triplicate and the values were averaged to calculate the weight of the filtered sample.
-the screens of the ZHE get clogged easily, and the filters disintegrate with grainy/sandy samples

Laboratory #3

The pistons in the ZHE have been designed too large such that they do not move freely, creating a lot of pressure in the vessel during introduction of the extraction fluid. This great pressure has resulted in the breakage of many expensive glass syringes. We suggest that even after the piston problem is fixed, possibly the use of stainless steel syringes can be promoted.

Laboratory #4

Sample 208 was extremely high in volatile organics and contaminated the GC/MS System; three days were required to decontaminate. Unfortunately, the TCLP extraction for Sample 208 was extracted first and contamination was found throughout the ZHE system for many days, including Sample 202 and extraction Blanks. Despite rinsing with methanol, and DI water, followed by oven bake-out, contamination was still present. Perhaps the O-rings and wiper seal retained small amounts of contamination over a long period of time, since they were not put in the oven.

4.0 CONCLUSIONS

The test results presented in the pevious sections lead to the following conclusions regarding the TCLP:

(1) The precision of the TCLP for the inorganic parameters tested is approximately the same as, or slightly better than that of the EP Toxicity procedure.(See Table 25, page 39)

(2) The TCLP is not a precise test, as illustrated by the following data excerpted from Tables 23 and 24 (pages 27 and 33):

Inorganics

Waste #	Parameter	%RSD
201	Barium	49
204	Barium	56
	Chromium	51
205	Barium	8.7
208	Barium	22
	Cadmium	18
	Lead	12
212	Arsenic	45
	Cadmium	16
	Chromium	20
	Lead	47
	Selenium	63
214	Cadmium	14
	Lead	7.4

Organics

208	1,1,1,2-Tetra-chloroethane	56
	1,1,2,2-Tetra-chloroethane	28
	1,1,2-Trichloro-ethane	24
	Trichloroethylene	78

These data show that the uncertainty in a TCLP result ranges from ±15% to ±234%, with an average uncertainty range of ±102% (based on a 99% confidence interval). In general terms, a TCLP value should be considered to be ±100%.

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(3) The reproducibility of the TCLP (inter-laboratory precision) is considerably worse than the repeatability (intra-laboratory precision).

(4) Lack of homogeneity of wastes and the resulting difficulty in obtaining representative samples are major contributors to the uncertainty surrounding TCLP values.

(5) The TCLP produces somewhat higher leachate concentrations of the inorganic parameters tested than does the EP Toxicity procedure. This is demonstrated by both the data on wastes tested (see Table 25) and the "spike recovery" data (see Table 27 and Figure 4)

(6) The acetate medium used in the TCLP is considerably more aggressive in leaching metals from wastes than is deionized water.

(7) Problems exist in use of the ZHE, primarily related to inconsistent piston operation and carryover of contaminants. The caryover problem is so severe that a waste can be falsely identified as leaching listed organics above the proposed regulatory levels. Work is needed on improvements to the device and/or handling procedures to improve consistency of operation and reduce carryover.

APPENDIX A

ERRATA

"Compilation of Phase IA and Phase II Data"

INTER-INDUSTRY TCLP STUDY

Phase II Data

Waste # 205

Parameter	Organics Detected - TCLP Leachate Semi-Volatiles (mg/l) Lab #1	Lab #2	Lab #3
Semi-Volatiles	NC	ND	ND

NC = Not complete; data not available as of 9/15/86
ND = Not detected; detection limits available with raw data

INTER-INDUSTRY TCLP STUDY

TCLP Phase II Data

Waste # 205

TCLP with DI Water

Parameter	Lab # 3 Organics Detected - TCLP Leachate Semi-volatiles, mg/l
Semi-volatiles	ND

ND = Not detected; detection limits available with raw data

INTER-INDUSTRY TCLP STUDY

Phase II Data

Waste # 208

Organics Detected
Volatiles

Parameter	Lab #4		Lab #5		Lab #6	
	Screen mg/kg	TCLP mg/l	Screen mg/kg	TCLP mg/l	Screen mg/kg	TCLP mg/l
1,2-Dichloroethane	ND	ND	250	7.5	NC	8.2
	ND	ND	NC	6.9	NC	7.8
		ND		8.3		7.8
1,1-Dichloroethylene	ND	ND	550	4.0	NC	ND
	ND	ND	NC	3.9	NC	ND
		ND		5.8		ND
Methylene chloride	3,900	62	1,600	5.0*	NC	ND
	1,700	ND	NC	3.2*	NC	ND
		ND		5.0*		5.2
Methyl ethyl ketone	ND	ND	8,400	2.8*	NC	ND
	ND	ND	NC	3.0*	NC	ND
		ND		3.0*		ND
1,1,1,2-Tetrachloroethane	35,000	330	33,000	660	NC	210
	34,000	270	NC	710	NC	210
		250		650		210
1,1,2,2-Tetrachloroethane	26,000	500	37,000	960	NC	560
	35,000	630	NC	920	NC	500
		650		840		510
Tetrachloroethylene	ND	ND	24,000	28	NC	ND
	ND	ND	NC	44	NC	ND
		ND		42		ND
1,1,1-Trichloroethane	ND	ND	280	0.55	NC	ND
	ND	ND	NC	0.90	NC	ND
		ND		0.82		ND
1,1,2-Trichloroethane	740	37	2,000	43		34
	800	17	NC	46	NC	34
		36		46	NC	34
Trichloroethylene	3,300	41	25,000*	75*	NC	49
	3,000	31	NC	150*	NC	45
		33		190*		44

*Contaminant found in blank extraction
ND = Not detected: Detection limits available with raw data
NC = Not complete: Data not available as of 9/15/86

APPENDIX B

PHASE IA SAMPLING PROTOCOL

TCLP PROJECT PHASE IA

GENERAL SAMPLING PROTOCOL

1.0 Sample Containers

1.1 Type: 1 liter glass, wide-mouth bottles with PTFE-lined screw caps

1.2 Number: Two (2) for each waste to be sampled

1.3 Labeling: Sampling containers are pre-labeled and identified with a code number before shipment to the point of sample collection.

1.4 Transport: Containers will be shipped in insulated cartons (Lancy CUSTOM-PAK's) via UPS or equivalent. CUSTOM-PAK's contain:

1) sample containers
2) envelopes with the following enclosures:

a. this sample protocol

b. shippinglabels with the address of the intended destination of the waste sample

c. sampling instructions

d. sampling record forms (chain-of-custody)

2.0 Sampling

2.1 Obtain subsamples from the waste according to site specific instructions included with thisprotocol. NOTE: Each subsample will be large enough to result in a composite of approximately 3 liters.

2.2 Combine subsamples in a 1 gallon bucket (plastic). Mix the combined subsamples by stirring or physically shaking the bucket, depending on the characteristics of the waste. Large chunks of sample should be broken into small (approximately 1/2") pieces, with a hammer if necessary, before the sample is mixed.

2.3 Complete the compositing/transfer of samples according to one of the following procedures, depending upon the nature of the waste.

a) Pour liquid, fluid, or finepowder samples directly into each of the two (2) sample containers. This transfer should be made quickly to keep dense solids from settling. Fill bottles to the shoulder, not full, to permit adequate mixing in the sample container.

b) Transfer solid samples, other than fine powders, as follows:

1. Spread the sample out on a polyethylene sheet and physically divide the sample into 4 equal sections.

2. Transfer approximately 50 ml of sample by filling a graduated or pre-marked glass container (e.g. 100 ml beaker) to the 50 ml mark with waste from one of the quarters and pour it into one of the sample containers.

3. Repeat this procedure with each successive quarter until the sample bottle is filled to the shoulder (approximately 4 samples/quarter).

2.4 Place the Sampling Record Forms, sampling modification and comments forms, and all documents related to site sampling in the envelope provided. Place the envelope in the plastic bag and seal it.

2.5 Place the filled sample containers and the plastic bag containing forms in the CUSTOM-PAK with appropriate packing material, affix label provided, and ship via UPS or equivalent carrier to the facility identified on pre-printed shipping labels provided.

TCLP PHASE IA

SITE SPECIFIC SAMPLING PROTOCOL

Waste #1

Sampling:

1. Follow the standard reverb slag sampling plan as scheduled.

2. In addition to the regular sample, collect one extra 9" x 12" bag from each of the first two sampling sites.

3. Break any large chunks of sample into small 1/2 inch pieces by striking the bags with a hammer.

4. Transfer the slag samples from the bags to a one gallon plastic bucket and proceed to Section 2.3 under the General Sampling Protocol.

TCLP PHASE IA

SITE SPECIFIC SAMPLING PROTOCOL

Waste #2

Sampling:

1. At random, pick one styrene pit to sample.

2. Divide the pit into 4 quadrants.

3. Using a chemically compatible section of pipe at least 3/4" diameter and long enough to sample the full depth of the pit, remove a core sample from the middle of the first quadrant and transfer to a chemically compatible one (1) gallon bucket.

4. Continue removing cores from the same quadrant until the bucket is approximately 1/4 full.

5. Repeat steps three (3) and (4) in the remaining three quadrants, collecting approximately one quart of sample at each location.

6. Proceed to 2.3 under the General Sampling Protocol.

TCLP PHASE IA

SITE SPECIFIC SAMPLING PROTOCOL

Waste #3

1. Sample Containers - Exceptions to General Sampling Protocol

   Type: 4 liter glass, wide-mouth bottle with PTFE-lined screw caps.
   Number: two (2) for each waste.

2. Sampling

   2.1 Obtain, at a minimum, 10 liters of composite sludge from the aerobic digestor and storage lagoons according to standard written sampling protocol for this facility from previous sampling of the waste.

   2.2 Transfer the composite sample to the two (2) 4-liter sample containers. This transfer should be made quickly to prevent dense solids from settling. Fill bottles to the shoulder, not full, to permit adequate mixing in the sample container.

   2.3 Cap the containers and wrap the lids with electrical tape to prevent spillage during transport.

   2.4 Proceed as directed in the General Sampling Protocol.

TCLP PHASE IA

SITE SPECIFIC SAMPLING PROTOCOL

Waste #4

Sampling:

1. Proceed to the area where the most recently produced furnace dust has been deposited.

2. Remove three (3) trowelsful from not less than ten (10) locations across the area of the recently deposited dust.

3. Proceed to Step 2.2 under the general sampling protocol.

Waste Source Code_____

TCLP PROJECT PHASE 1A

Sampling Record

Waste Type:_____

Waste Source:_____

Sample Taken By:_____ Date_____

Witness To Sampling:_____ Date_____

Sample Shipped Via:_____ Date_____

Sample Shipment Prepared By:_____

Comments:

For Lancy Laboratories Use Only

Custodian:_____ Date Received_____

Sample Shipped for Analysis Via:_____ Date_____

Sample Shipment Prepared By:_____

Comments:

TCLP PROJECT PHASE 1A

Sampling Modifications and Comments

List Modifications to Sampling Protocol Below:

Additional Comments:

APPENDIX C

PHASE IA LABORATORY PROTOCOL

TCLP Project Phase IA
General Laboratory Protocol

1.0 Chain-of-Custody

Follow standard chain-of-custody procedures employed in your laboratory to ensure sample integrity. In addition:

- Initiate Phase IA Data Sheets for each sample received.
- Maintain all raw data associated with TCLP, EP, and analyses.

2.0 Blanks & Duplicates

Duplicate determinations will be made in Phase IA. For each sample that you receive, perform two (2) separate EP Toxicity tests and two (2) separate TCLP tests, following the procedure described below. Follow the protocol with respect to blanks.

3.0 Procedure

3.1 EP Toxicity

Follow Method 1310 from SW-846. Analyze extract for:

Arsenic	Lead
Barium	Mercury
Cadmium	Selenium
Chromium	

Use the analytical methods given in Table 1, employing standard additions as specified in 1310.

3.2 TCLP

Follow new draft protocol (copy attached) excluding sections related to volatiles. Analyze extract for:

Arsenic	Lead	*plus phenols
Barium	Mercury	Total Organic Halogen
Cadmium	Selenium	
Chromium	Selenium	

Use the analytical methods given in Table 1, employing standard additions as specified in the protocol.

*Phenols and cresols are expected to be present in Waste #0006; organic content of Wastes #0002, 0003, and 0005 is unknown; Wastes 0001 and 0004 do not contain organics and do not require analysis for organics.

4.0 Data

Perform calculations as directed in each of the two test methods. Report data on Phase IA Data Sheets. For each sample you will receive one set containing two EP TOX and two TCLP data sheets. In addition, please include discussion of all aspects of the procedures in detail. Your observations and comments are vital to the success of this project.

Table 1. Methods of Analysis

Parameter	EPA Method No.
Arsenic	7060, 7061
Barium	7080, 6010
Cadmium	7130, 6010
Chromium	7190, 6010
Lead	7420, 6010
Mercury	7470
Selenium	7740, 7741
Metals Digestion	3010, 3020
Phenols	420.1, 420.2
Total Organic Halogen	9020

These represent the parameters to be analyzed for each extract and the particular methods to be followed. If more than one method number is listed, the choice is left to the analyst. Please note that all metal determinations must be made on digested extracts. The particular digestion is determined by the specific method for each parameter.

Quality Control

1. The method of standard additions shall be used as called for in the test protocols.

2. An analytical blank is required with each set of analyses. Follow EP TOX and TCLP Protocol for other aspects of QA.

3. Quality assurance practices for organic analysis are specified in the listed methodology.

TCLP PROJECT

Phase IA Data Sheet

Laboratory # _____

Waste # _____ Date Received _____

Physical State: Solid _____ Liquid _____ "Semi-Solid" _____

Multiphase? (Describe) _____

Comments: _____

Partical Size Reduction Required? (Circle One) Yes No

If yes, briefly describe the procedure:

_____

_____

_____

_____

Apparatus

Rotary Extraction Apparatus:

Identify any deviation from standard dimensions/operation

_____

_____

_____

_____

Extraction Vessels:

Describe containers used

_____

_____

_____

_____

Filtration Apparatus:

Identify apparatus used

_____

_____

Reagents

Water:

Identify source of Type 1 water:

TCLP Extraction Fluid:

Selection Test Results - Step 7.12.2 pH____ Step 7.12.4 pH____
Extraction Fluid (circle one) #1 #2

EP PROCEDURE

Waste #_____ RUN #1

Initial Separation Required (Circle One) Yes No

If Yes: gm of initial sample filtered_____gm
gm of total filtrate_____gm
volume of total filtrate_____ml
gm of total solid_____gm

gm of solid leached	_____	gm
ml of DI water initially added	_____	ml
ml of 0.5N acetic acid added	_____	ml
ml of DI water added on completion	_____	ml
ml of filtrate added (if applicable)	_____	ml
Initial pH of extract	_____	s.u.
Final pH of extract	_____	s.u.

Date EP Started_____

Parameter	Result mg/L	Date	Sample Prep. Method	Analytical Method #	Analyst Initials
Arsenic	_____	_____	_____	_____	_____
Barium	_____	_____	_____	_____	_____
Cadmium	_____	_____	_____	_____	_____
Chromium	_____	_____	_____	_____	_____
Lead	_____	_____	_____	_____	_____
Mercury	_____	_____	_____	_____	_____
Selenium	_____	_____	_____	_____	_____

EP PROCEDURE

Waste #_____ RUN #2

Initial Separation Required (Circle One) Yes No

If Yes: gm of initial sample filtered_____gm
gm of total filtrate_____gm
volume of total filtrate_____ml
gm of total solid_____gm

gm of solid leached	_____	gm
ml of DI water initially added	_____	ml
ml of 0.5N acetic acid added	_____	ml
ml of DI water added on completion	_____	ml
ml of filtrate added (if applicable)	_____	ml
Initial pH of extract	_____	s.u.
Final pH of extract	_____	s.u.

Date EP Started_____

Parameter	Result mg/L	Date	Sample Prep. Method	Analytical Method #	Analyst Initials
Arsenic					
Barium					
Cadmium					
Chromium					
Lead					
Mercury					
Selenium					

TCLP PROCEDURE

Waste #_____ RUN #1

Initial separation Required (Circle One) Yes No

If Yes: gm of initial sample filtered _____ gm
gm of total filtrate _____ gm
volume of total filtrate _____ ml
gm of total solid _____ gm

gm of solid leached _____ gm
ml of buffer added _____ ml
ml of filtrate added (if applicable) _____ ml
Initial pH of extract _____ s.u.
Final pH of extract _____ s.u.

Date TCLP Started_____

Parameter	Result mg/L	Date	Sample Prep. Method	Analytical Method #	Analyst Initials
Arsenic					
Barium					
Cadmium					
Chromium					
Lead					
Mercury					
Selenium					
Acid Extractable Organics:	ug/L				
Phenols (Total)					
Pentachlorophenol					

Attach data on any other organics identified or quantitated.

TOX ___

TCLP PROCEDURE

Waste #_____ RUN #2

Initial Separation Required (Circle One) Yes No

If Yes: gm of initial sample filtered_____gm
gm of total filtrate_____gm
volume of total filtrate_____ml
gm of total solid_____gm

gm of solid leached _____ gm
ml of buffer added _____ ml
ml of filtrate added (if applicable) _____ ml
Initial pH of extract _____ s.u.
Final pH of extract _____ s.u.

Date TCLP Started_____

Parameter	Result mg/L	Date	Sample Prep. Method	Analytical Method #	Analyst Initials
Arsenic					
Barium					
Cadmium					
Chromium					
Lead					
Mercury					
Selenium					
Acid Extractable Organics:	ug/L				
Phenols (Total)					
Pentachlorophenol					

Attach data on any other organics identified or quantitated.

TOX ___

Comments and Observations:

Date:_____

Submitted by_____

_____

APPENDIX D

PHASE II SAMPLING PROTOCOL

TCLP PROJECT PHASE IA

GENERAL SAMPLING PROTOCOL

1.0 Sample Containers

1.1 Type: 1 liter glass, wide-mouth bottles with PTFE-lined screw caps

1.2 Number: Two (2) for each waste to be sampled

1.3 Labeling: Sampling containers are pre-labeled and identified with a code number before shipment to the point of sample collection.

1.4 Transport: Containers will be shipped in insulated cartons (Lancy CUSTOM-PAK's) via UPS or equivalent. CUSTOM-PAK's contain:

1) sample containers
2) envelopes with the following enclosures:

a. this sample protocol

b. shippinglabels with the address of the intended destination of the waste sample

c. sampling instructions

d. sampling record forms (chain-of-custody)

2.0 Sampling

2.1 Obtain subsamples from the waste according to site specific instructions included with thisprotocol. NOTE: Each subsample will be large enough to result in a composite of approximately 3 liters.

2.2 Combine subsamples in a 1 gallon bucket (plastic). Mix the combined subsamples by stirring or physically shaking the bucket, depending on the characteristics of the waste. Large chunks of sample should be broken into small (approximately 1/2") pieces, with a hammer if necessary, before the sample is mixed.

2.3 Complete the compositing/transfer of samples according to one of the following procedures, depending upon the nature of the waste.

a) Pour liquid, fluid, or finepowder samples directly into each of the two (2) sample containers. This transfer should be made quickly to keep dense solids from settling. Fill bottles to the shoulder, not full, to permit adequate mixing in the sample container.

b) Transfer solid samples, other than fine powders, as follows:

1. Spread the sample out on a polyethylene sheet and physically divide the sample into 4 equal sections.

2. Transfer approximately 50 ml of sample by filling a graduated or pre-marked glass container (e.g. 100 ml beaker) to the 50 ml mark with waste from one of the quarters and pour it into one of the sample containers.

3. Repeat this procedure with each successive quarter until the sample bottle is filled to the shoulder (approximately 4 samples/quarter).

2.4 Place the Sampling Record Forms, sampling modification and comments forms, and all documents related to site sampling in the envelope provided. Place the envelope in the plastic bag and seal it.

2.5 Place the filled sample containers and the plastic bag containing forms in the CUSTOM-PAK with appropriate packing material, affix label provided, and ship via UPS or equivalent carrier to the facility identified on pre-printed shipping labels provided.

SITE SPECIFIC SAMPLING INSTRUCTIONS
WASTE #201

Volatiles Involved ___X___ Yes _____ No

Follow routine sampling procedures for disposal monitoring with the following inclusions:

1. Pump sludge from four (4) discrete sample points in the lagoon.

2. Fill one (1) container at each sample point.

3. Pump sludge for at least three (3) minutes before filling each sample container.

SITE SPECIFIC SAMPLING INSTRUCTIONS
WASTE #202

Volatiles Involved ___X___ Yes _____ No

1. Sample the drying beds with a soil core sampler capable of sampling the entire depth of the beds.

2. Randomly select four (4) sampling points from each of the six (6) lagoons.

3. Calculate the volume removed with one (1) core sample.

4. Determine the number of core samples required to fill the gallon container.

5. Divide the number of core samples determined in Step 4 by 24 and remove that number of cores at each sample point.

6. Transfer the core samples as quickly as possible to the cold sample container. Remove the lid only to add sample and replace it quickly.

7. At the final sample point, add enough sample to completely fill the sample container. Avoid air head space or entrapment as practically possible.

SITE SPECIFIC SAMPLING INSTRUCTIONS
WASTE #203

Volatiles Involved ____X___Yes _____No

1. Randomly select four (4) sampling points from each of the three drying beds.

2. Rapidly sample and transfer approximately one (1) quart of sample from the first sample point to the cold gallon container. DO NOT remove the container from the chest.

3. Repeat Step two (2) for the next three (3) sample points.

4. At sample point four (4) of the first drying bed add enough sample to fill the first gallon container completly.

5. Repeat Steps 2-4 for the remaining two (2) drying beds. (The result should be 3 filled gallon bottles each containing 1 gallon from 1 drying bed).

6. Record the location of the sampling points for future reference.

7. Briefly describe the sampling method on the enclosed forms.

SITE SPECIFIC SAMPLING INSTRUCTIONS
WASTE #204

Volatiles Involved ___X___ Yes _____ No

Follow in-house waste sampling protocol from routine sampling with the following inclusions:

1. Obtain one (1) gallon of waste from each quadrant of the "Greenbelt" area. Remove enough core sample from each sample point in the quadrant to insure the gallon container will be filled completely.

2. Do not combine the four (4) 1 gallon containers following collection.

3. Record the various core locations for future reference and return the samples.

SITE SPECIFIC SAMPLING INSTRUCTIONS
WASTE #205

Volatiles Involved _____Yes ____X___No

1. Decant the supernate from the clarified waste sample.

2. Mix the remaining sludge with the desired solid contents to insure representativeness.

3. Transfer the well mixed material to the four (4) 1 gallon containers as described in the general sampling protocol.

4. Briefly describe the sampling procedure used to obtain the original liquid sample on the enclosed forms.

SITE SPECIFIC SAMPLING INSTRUCTIONS
WASTE #206

Volatiles Involved _____Yes ___X___No

Follow previous waste sampling procedures with the following inclusions:

1. Remove, at a minimum, 10 sub-samples of waste from 10 randomly selected sampling points in the silo.

2. Include subsamples from different depths, if possible, in an effort to profine the vertical aspects of the waste and storage silo.

3. Record the actual sub-sample locations for future reference.

4. Provide a brief description of the actual sampling procedures on the enclosed forms.

SITE SPECIFIC SAMPLING INSTRUCTIONS
WASTE #207

Volatiles Involved _____Yes ____X___No

Follow previous waste sampling procedures with the following inclusions:

1. Remove, at a minimum, 10 subsamples of waste from 10 randomly selected sampling points across the surface area of the lagoon.

2. If waste depths are not prohibitive, remove core samples which represent the complete vertical profile of the lagoon. If impractical, remove subsamples from different depths of the lagoons to approximate this vertical profile.

3. Record the actual subsample locations for future reference.

4. Provide a brief description of the actual sampling procedures on the enclosed forms.

SITE SPECIFIC SAMPLING INSTRUCTIONS
WASTE #208 (Drum #1)

Volatiles Involved ___X___ Yes _____ No

1. Remove representative subsamples from various depths of the waste drum and transfer them rapidly to the cold sample container.

2. The sample container must be filled completely with waste.

3. Record the Lancy waste number on the sampled waste drum for future reference.

4. Briefly describe the waste transfer procedure on the enclosed forms.

SITE SPECIFIC SAMPLING INSTRUCTIONS
WASTE #209 (Drum #2)
SEE WASTE #208

SITE SPECIFIC SAMPLING INSTRUCTIONS
WASTE #212

Volatiles Involved _____Yes ___X___No

Follow in-house waste sampling protocol from previous sampling events with the following inclusions:

1. Composite sludge from four (4) sludge cakes (two (2) from each press). If more sludge is required to composite one (1) gallon, use additional cakes from each press.

2. Record the time of each press run from which cake was removed.

3. Briefly describe the sampling procedure on the enclosed forms.

SITE SPECIFIC SAMPLING INSTRUCTIONS
WASTE #213

Volatiles Involved _____Yes ____X___No

Follow in-house sampling protocol from previous sampling events with the following inclusions:

1. Remove subsamples from at least 10 randomly selected points behind the dam.

2. Combine these subsamples as described in the general sampling protocol.

3. Record the location of the sampling points for future reference.

4. Briefly describe the sampling procedure on the enclosed forms.

SITE SPECIFIC SAMPLING INSTRUCTIONS
WASTE #214

Volatiles Involved _____Yes ___X___No

Follow sampling procedures from previous sampling events with the following inclusions:

1. Remove at least 10 sub-samples from at least 10 randomly selected points on a dryer section of the holding area.

2. Combine and transfer subsamples as specified in the general sampling protocol.

3. Record the various sampling points for future reference and return the samples to Lancy.

SITE SPECIFIC SAMPLING INSTRUCTIONS
WASTE #215

Volatiles Involved _____Yes ___X___No

1. Select an area of interest containing waste recently disposed
2. Randomly select 10 sampling points in the area of interest.
3. Remove equal volumes of waste from the 10 sampling points using techniques from previous sampling events.
4. Combine and transfer the subsamples as described in the general sampling instructions.
5. Record the sampling points for future reference.
6. Breifly describe the sampling method on the enclosed forms.

APPENDIX E

PHASE II LABORATORY PROTOCOL

TCLP Project Phase II
General Laboratory Protocol

1.0 Chain-of-Custody

Follow standard chain-of-custody procedures employed in your laboratory to ensure sample integrity. In addition:

- o Initiate Phase II Data Sheets for each sample received.
- o Maintain all raw data associated with TCLP, EP, and DI analyses.

2.0 Blanks & Duplicates

Duplicate determinations will be made in Phase II. For each sample received, perform two (2) separate extractions for each required leaching procedure. Follow the TCLP/EP protocol with respect to blanks.

3.0 Spikes

Spiked extractions will be prepared and analyzed in Phase II. For each sample received, spike one (1) extraction, following procedures listed in Section 4, for each required leaching procedure. This results in a total of three (3) separate extractions/waste received.

4.0 Procedure

4.1 Determine thr required extractions and analyses for each waste sample from the waste - specific protocol. Please note: not all wastes require the same extractions or analyses. Please read waste - specific protocols carefully.

4.2 TCLP With ZHE

4.2.1 Volatile Organics Screen: Analyze the waste for volatile organics using methods specified in Table I. If no volatile compounds listed on Data Sheet #2 are quantified at >1 mg/kg, contact Philip Fatula at Lancy (412/452-9360) for further instructions. These screens must be performed in duplicate.

4.2.2 Follow the proposed TCLP Procedure when volatiles are involved. Analyze the extracts for volatile organics using methods specified in Table I.

4.2.3 S]pike one of the three TCLP extracts prior to extraction by injecting 0.50 ml of Solution A directly into the ZHE. Inject Solution A through the extraction fluid port using a luer-type syringe after all but 50 ml of extraction fluid has been added. Add the last 50 ml of extraction fluid after the spike injection and pressurize the ZHE.

4.3 TCLP Without ZHE

4.3.1 Follow the proposed TCLP procedure when volatiles are not involved. Analyze the extracts for semi-volatiles and/or inorganics using methods specified in Table I.

4.3.2 If the waste is a precision study sample to be tested for semi-volatile compounds as identified in the waste specific protocol, spike one of the three extracts with semi-volatile compounds by adding 1.0 ml of solution B directly to the extraction vessel after the solids and extraction fluid have been added.

4.3.3 If the waste is not a precision study sample but is none-the-less to be analyzed for semi-volatile mobility, spike one of the three extracts with semi-volatile compounds by adding 1.0 ml of solution C directly to the filtered or obviously dry solids which are to be leached. Add the solution to the solids in a fume hood and mix thoroughly. Let the sample sit for 15 minutes in the hood and then transfer the solids to the extraction vessel.

4.3.4 If the waste is to be tested for inorganic mobility as identified in the waste - specific protocol, spike one of the three extracts with inorganic compounds by pipeting 1.0 ml of solution D directly into the extraction vessel after the solids and extraction fluid have been added.

4.3.5 If both semi-volatile and inorganic compounds are required for a specific waste, separate spiked extractions need not be performed for each group. Spike the same extraction with both solutions.

4.4 EP

4.4.1 Follow EPA SW-846 Method 1310 for the preparation of EP extracts. Analyze the extracts for inorganics only using methods specified in Table I.

4.4.2 Spike one of the three EP extracts with inorganics as described in Section 4.3.4 for TCLP extracts.

4.5 DI With ZHE

4.5.1 Follow the proposed TCLP procedure when volatiles are involved. Substitute ASTM Type I or equivalent deionized water for the extraction fluid used in the TCLP procedure. Analyze the extracts for volatile organics using methods specified in Table I.

4.5.2 Spike one of the three DI water extracts with volatile compounds as described in Section 4.2.3 for TCLP extracts.

4.6 DI Without ZHE

4.6.1 Follow the proposed TCLP procedure when volatiles are not involved. Substitute ASTM Type 2 or equivalent deionized water for the extraction fluid used in the TCLP procedure. Analyze the extracts for semi-volatiles and/or inorganics using methods specified in Table I.

4.6.2 Spike one of the three DI water extracts with semi-volatiles and/or inorganics as described in Section 4.3.3 through 4.3.5.

5.0 Data

5.1 Perform calculations as directed in the test procedures. For each sample, you will receive one set of data sheets. Report results for the various extracts on the appropriate sheets.

5.2 The data sheets list only toxicity characteristic contaminants. If other organic compounds are quantified during the course of analysis, please report these data on your routine laboratory report forms and attach them to the data package.

5.3 All QA/QC data associated with these analyses should be retained in your files. It will not be necessary to include QC data with your results at this time, but these data may be requested during the data evaluation stage of the project.

TCLP PROJECT

Phase II Data Sheet

Laboratory # _____

Waste # _____ Date Received _____

Physical State: Solid _____ Liquid _____ "Semi-Solid" _____

Multiphase? (Describe) _____

Comments: _____

Partical Size Reduction Required? (Circle One) Yes No

If yes, briefly describe the procedure:

_____

_____

_____

_____

Apparatus

Rotary Extraction Apparatus:

Identify any deviation from standard dimensions/operation

_____

_____

_____

_____

Extraction Vessels:

Describe containers used

_____

_____

_____

_____

Filtration Apparatus:

Identify apparatus used

_____

_____

Reagents

Water:

Identify source of Type 1 water:

TCLP Extraction Fluid:

Selection Test Results - Step 7.12.2 pH____ Step 7.12.4 pH____
Extraction Fluid (circle one) #1 #2

TCLP PROCEDURE
Volatile Screen

Waste #_____ RUN #1 Analyst's Initials

Date of Analysis _____ _____

Method Code _____ _____ _____

Parameter	Result (ug/l)
1. Acrylonitrile	_____
2. Benzene	_____
3. Carbon disulfide	_____
4. Carbon tetrachloride	_____
5. Chlorobenzene	_____
6. Chloroform	_____
7. 1,2-Dichloroethane	_____
8. 1,1-Dichloroethylene	_____
9. Isobutanol	_____
10. Methylene chloride	_____
11. Methyl ethyl ketone	_____
12. Pyridine	_____
13. 1,1,1,2-Tetrachloroethane	_____
14. 1,1,2,2-Tetrachloroethane	_____
15. Tetrachloroethylene	_____
16. Toluene	_____
17. 1,1,1-Trichloroethane	_____
18. 1,1,2-Trichloroethane	_____
19. Trichloroethylene	_____
20. Vinyl chloride	_____

TCLP PROCEDURE
Volatile Screen

Waste #_____ RUN #2 Analyst's Initials

Date of Analysis _____ _____

Method Code _____ _____ _____

	Parameter	Result (ug/l)
1.	Acrylonitrile	_____
2.	Benzene	_____
3.	Carbon disulfide	_____
4.	Carbon tetrachloride	_____
5.	Chlorobenzene	_____
6.	Chloroform	_____
7.	1,2-Dichloroethane	_____
8.	1,1-Dichloroethylene	_____
9.	Isobutanol	_____
10.	Methylene chloride	_____
11.	Methyl ethyl ketone	_____
12.	Pyridine	_____
13.	1,1,1,2-Tetrachloroethane	_____
14.	1,1,2,2-Tetrachloroethane	_____
15.	Tetrachloroethylene	_____
16.	Toluene	_____
17.	1,1,1-Trichloroethane	_____
18.	1,1,2-Trichloroethane	_____
19.	Trichloroethylene	_____
20.	Vinyl chloride	_____

TCLP PROCEDURE
Volatiles (ZHE)

Waste # _____ RUN #1 Analyst's Initials

Date TCLP Started _____ _____

Date(s) Volatiles Analysis _____ _____

Initial Weight of Sample _____ gm
Weight of Filtrate _____ gm
Weight of Solids _____ gm
Volume of Extration Fluid _____ ml
Liquid Phases Combined: (Circle One) Physically Mathematically

	Parameter	Result (ug/l)
1.	Acrylonitrile	_____
2.	Benzene	_____
3.	Carbon disulfide	_____
4.	Carbon tetrachloride	_____
5.	Chlorobenzene	_____
6.	Chloroform	_____
7.	1,2-Dichloroethane	_____
8.	1,1-Dichloroethylene	_____
9.	Isobutanol	_____
10.	Methylene chloride	_____
11.	Methyl ethyl ketone	_____
12.	Pyridine	_____
13.	1,1,1,2-Tetrachloroethane	_____
14.	1,1,2,2-Tetrachloroethane	_____
15.	Tetrachloroethylene	_____
16.	Toluene	_____
17.	1,1,1-Trichloroethane	_____
18.	1,1,2-Trichloroethane	_____
19.	Trichloroethylene	_____
20.	Vinyl chloride	_____

TCLP PROCEDURE
Volatiles (ZHE)

Waste #_____ RUN #2 Analyst's Initials

Date TCLP Started _____ _____

Date(s) Volatiles Analysis _____ _____

Initial Weight of Sample _____gm
Weight of Filtrate _____gm
Weight of Solids _____gm
Volume of Extration Fluid _____ml
Liquid Phases Combined: (Circle One) Physically Mathematically

	Parameter	Result (ug/l)
1.	Acrylonitrile	
2.	Benzene	
3.	Carbon disulfide	
4.	Carbon tetrachloride	
5.	Chlorobenzene	
6.	Chloroform	
7.	1,2-Dichloroethane	
8.	1,1-Dichloroethylene	
9.	Isobutanol	
10.	Methylene chloride	
11.	Methyl ethyl ketone	
12.	Pyridine	
13.	1,1,1,2-Tetrachloroethane	
14.	1,1,2,2-Tetrachloroethane	
15.	Tetrachloroethylene	
16.	Toluene	
17.	1,1,1-Trichloroethane	
18.	1,1,2-Trichloroethane	
19.	Trichloroethylene	
20.	Vinyl chloride	

TCLP PROCEDURE
Volatiles (ZHE)

Waste #_____ SPIKE — Analyst's Initials
Date TCLP Started _____ _____
Date(s) Volatiles Analysis _____ _____

Initial Weight of Sample _____gm
Weight of Filtrate _____gm
Weight of Solids _____gm
Volume of Extration Fluid _____ml
Liquid Phases Combined: (Circle One) Physically Mathematically

Parameter	Result (ug/l)
1. Acrylonitrile	
2. Benzene	
3. Carbon disulfide	
4. Carbon tetrachloride	
5. Chlorobenzene	
6. Chloroform	
7. 1,2-Dichloroethane	
8. 1,1-Dichloroethylene	
9. Isobutanol	
10. Methylene chloride	
11. Methyl ethyl ketone	
12. Pyridine	
13. 1,1,1,2-Tetrachloroethane	
14. 1,1,2,2-Tetrachloroethane	
15. Tetrachloroethylene	
16. Toluene	
17. 1,1,1-Trichloroethane	
18. 1,1,2-Trichloroethane	
19. Trichloroethylene	
20. Vinyl chloride	

TCLP PROCEDURE
Inorganics

Waste #_____ RUN #1

Initial separation Required (Circle One) Yes No

If Yes: gm of initial sample filtered _____ gm
gm of total filtrate _____ gm
volume of total filtrate _____ ml
gm of total solid _____ gm

gm of solid leached _____ gm
ml of buffer added _____ ml
ml of filtrate added (if applicable) _____ ml
Initial pH of extract _____ s.u.
Final pH of extract _____ s.u.

Date TCLP Started_____

Parameter	Result mg/L	Date	Sample Prep. Method	Analytical Method #	Analyst Initials
Arsenic					
Barium					
Cadmium					
Chromium					
Lead					
Mercury					
Selenium					

TCLP PROCEDURE
Inorganics

Waste #_____ RUN #2

Initial separation Required (Circle One) Yes No

If Yes: gm of initial sample filtered _____ gm
gm of total filtrate _____ gm
volume of total filtrate _____ ml
gm of total solid _____ gm

gm of solid leached _____ gm
ml of buffer added _____ ml
ml of filtrate added (if applicable) _____ ml
Initial pH of extract _____ s.u.
Final pH of extract _____ s.u.

Date TCLP Started_____

Parameter	Result mg/L	Date	Sample Prep. Method	Analytical Method #	Analyst Initials
Arsenic					
Barium					
Cadmium					
Chromium					
Lead					
Mercury					
Selenium					

TCLP PROCEDURE
Inorganics

Waste #_____ SPIKE

Initial separation Required (Circle One) Yes No

If Yes: gm of initial sample filtered _____ gm
gm of total filtrate _____ gm
volume of total filtrate _____ ml
gm of total solid _____ gm

gm of solid leached _____ gm
ml of buffer added _____ ml
ml of filtrate added (if applicable) _____ ml
Initial pH of extract _____ s.u.
Final pH of extract _____ s.u.

Date TCLP Started_____

Parameter	Result mg/L	Date	Sample Prep. Method	Analytical Method #	Analyst Initials
Barium					
Cadmium					
Chromium					
Lead					

TCLP PROCEDURE
Semi-Volatiles

Waste #_____ RUN #1 Analyst's Initials

Date TCLP Started _____ _____

Date Acid Extractable Clean-up _____ _____

Date(s) Methylene Chloride Extraction _____ _____

Date(s) of Acid Extractables Analysis _____ _____

Date(s) of Base/Neutrals Analysis _____ _____

Parameter	Result (ug/l)
1. Bis(2-chloroethyl)ether	
2. Cresols (total)	
3. 1,2-Dichlorobenzene	
4. 1,4-Dichlorobenzene	
5. 2,4-Dinitrotoluene	
6. Hexachlorobenzene	
7. Hexachlorobutadiene	
8. Hexachloroethane	
9. Nitrobenzene	
10. Pentachlorophenol	
11. Phenol	
12. 2,3,4,6-Tetrachlorophenol	
13. 2,4,5-Trichlorophenol	
14. 2,4,6-Trichlorophenol	

TCLP PROCEDURE
Semi-Volatiles

Waste #_____ RUN #2 Analyst's Initials

Date TCLP Started _____ _____

Date Acid Extractable Clean-up _____ _____

Date(s) Methylene Chloride Extraction _____ _____

Date(s) of Acid Extractables Analysis _____ _____

Date(s) of Base/Neutrals Analysis _____ _____

	Parameter	Result (ug/l)
1.	Bis(2-chloroethyl)ether	
2.	Cresols (total)	
3.	1,2-Dichlorobenzene	
4.	1,4-Dichlorobenzene	
5.	2,4-Dinitrotoluene	
6.	Hexachlorobenzene	
7.	Hexachlorobutadiene	
8.	Hexachloroethane	
9.	Nitrobenzene	
10.	Pentachlorophenol	
11.	Phenol	
12.	2,3,4,6-Tetrachlorophenol	
13.	2,4,5-Trichlorophenol	
14.	2,4,6-Trichlorophenol	

TCLP PROCEDURE
Semi-Volatiles

Waste #_____ SPIKE Analyst's Initials

Date TCLP Started _____ _____

Date Acid Extractable Clean-up _____ _____

Date(s) Methylene Chloride Extraction _____ _____

Date(s) of Acid Extractables Analysis _____ _____

Date(s) of Base/Neutrals Analysis _____ _____

Parameter	Result (ug/l)
1. Bis(2-chloroethyl)ether	
2. Cresols (total)	
3. 1,2-Dichlorobenzene	
4. 1,4-Dichlorobenzene	
5. 2,4-Dinitrotoluene	
6. Hexachlorobenzene	
7. Hexachlorobutadiene	
8. Hexachloroethane	
9. Nitrobenzene	
10. Pentachlorophenol	
11. Phenol	
12. 2,3,4,6-Tetrachlorophenol	
13. 2,4,5-Trichlorophenol	
14. 2,4,6-Trichlorophenol	

EP PROCEDURE

Waste #_____ RUN #1

Initial Separation Required (Circle One) Yes No

If Yes: gm of initial sample filtered_____gm
gm of total filtrate_____gm
volume of total filtrate_____ml
gm of total solid_____gm

gm of solid leached	_____	gm
ml of DI water initially added	_____	ml
ml of 0.5N acetic acid added	_____	ml
ml of DI water added on completion	_____	ml
ml of filtrate added (if applicable)	_____	ml
Initial pH of extract	_____	s.u.
Final pH of extract	_____	s.u.

Date EP Started_____

Parameter	Result mg/L	Date	Sample Prep. Method	Analytical Method #	Analyst Initials
Arsenic	_____	_____	_____	_____	_____
Barium	_____	_____	_____	_____	_____
Cadmium	_____	_____	_____	_____	_____
Chromium	_____	_____	_____	_____	_____
Lead	_____	_____	_____	_____	_____
Mercury	_____	_____	_____	_____	_____
Selenium	_____	_____	_____	_____	_____

EP PROCEDURE

Waste #_____ RUN #2

Initial Separation Required (Circle One) Yes No

If Yes: gm of initial sample filtered_____gm
gm of total filtrate_____gm
volume of total filtrate_____ml
gm of total solid_____gm

gm of solid leached	_____	gm
ml of DI water initially added	_____	ml
ml of 0.5N acetic acid added	_____	ml
ml of DI water added on completion	_____	ml
ml of filtrate added (if applicable)	_____	ml
Initial pH of extract	_____	s.u.
Final pH of extract	_____	s.u.

Date EP Started_____

Parameter	Result mg/L	Date	Sample Prep. Method	Analytical Method #	Analyst Initials
Arsenic					
Barium					
Cadmium					
Chromium					
Lead					
Mercury					
Selenium					

EP PROCEDURE

Waste #_____ SPIKE

Initial Separation Required (Circle One) Yes No

If Yes: gm of initial sample filtered_____gm
gm of total filtrate_____gm
volume of total filtrate_____ml
gm of total solid_____gm

gm of solid leached	_____	gm
ml of DI water initially added	_____	ml
ml of 0.5N acetic acid added	_____	ml
ml of DI water added on completion	_____	ml
ml of filtrate added (if applicable)	_____	ml
Initial pH of extract	_____	s.u.
Final pH of extract	_____	s.u.

Date EP Started_____

Parameter	Result mg/L	Date	Sample Prep. Method	Analytical Method #	Analyst Initials
Barium	_____	_____	_____	_____	_____
Cadmium	_____	_____	_____	_____	_____
Chromium	_____	_____	_____	_____	_____
Lead	_____	_____	_____	_____	_____

DI PROCEDURE
Volatiles (ZHE)

Waste #_____ RUN #1 Analyst's Initials

Date TCLP Started _____ _____

Date(s) Volatiles Analysis _____ _____

Initial Weight of Sample _____gm
Weight of Filtrate _____gm
Weight of Solids _____gm
Volume of Extration Fluid _____ml
Liquid Phases Combined: (Circle One) Physically Mathematically

	Parameter	Result (ug/l)
1.	Acrylonitrile	
2.	Benzene	
3.	Carbon disulfide	
4.	Carbon tetrachloride	
5.	Chlorobenzene	
6.	Chloroform	
7.	1,2-Dichloroethane	
8.	1,1-Dichloroethylene	
9.	Isobutanol	
10.	Methylene chloride	
11.	Methyl ethyl ketone	
12.	Pyridine	
13.	1,1,1,2-Tetrachloroethane	
14.	1,1,2,2-Tetrachloroethane	
15.	Tetrachloroethylene	
16.	Toluene	
17.	1,1,1-Trichloroethane	
18.	1,1,2-Trichloroethane	
19.	Trichloroethylene	
20.	Vinyl chloride	

DI PROCEDURE
Volatiles (ZHE)

Waste #_____ RUN #2 Analyst's Initials

Date TCLP Started_____ _____

Date(s) Volatiles Analysis_____ _____

Initial Weight of Sample _____gm
Weight of Filtrate _____gm
Weight of Solids _____gm
Volume of Extration Fluid _____ml
Liquid Phases Combined: (Circle One) Physically Mathematically

Parameter	Result (ug/l)
1. Acrylonitrile	_____
2. Benzene	_____
3. Carbon disulfide	_____
4. Carbon tetrachloride	_____
5. Chlorobenzene	_____
6. Chloroform	_____
7. 1,2-Dichloroethane	_____
8. 1,1-Dichloroethylene	_____
9. Isobutanol	_____
10. Methylene chloride	_____
11. Methyl ethyl ketone	_____
12. Pyridine	_____
13. 1,1,1,2-Tetrachloroethane	_____
14. 1,1,2,2-Tetrachloroethane	_____
15. Tetrachloroethylene	_____
16. Toluene	_____
17. 1,1,1-Trichloroethane	_____
18. 1,1,2-Trichloroethane	_____
19. Trichloroethylene	_____
20. Vinyl chloride	_____

DI PROCEDURE
Volatiles (ZHE)

Waste # _____ SPIKE — Analyst's Initials
Date TCLP Started _____ _____
Date(s) Volatiles Analysis _____ _____

Initial Weight of Sample _____ gm
Weight of Filtrate _____ gm
Weight of Solids _____ gm
Volume of Extration Fluid _____ ml
Liquid Phases Combined: (Circle One) Physically Mathematically

Parameter	Result (ug/l)
1. Acrylonitrile	
2. Benzene	
3. Carbon disulfide	
4. Carbon tetrachloride	
5. Chlorobenzene	
6. Chloroform	
7. 1,2-Dichloroethane	
8. 1,1-Dichloroethylene	
9. Isobutanol	
10. Methylene chloride	
11. Methyl ethyl ketone	
12. Pyridine	
13. 1,1,1,2-Tetrachloroethane	
14. 1,1,2,2-Tetrachloroethane	
15. Tetrachloroethylene	
16. Toluene	
17. 1,1,1-Trichloroethane	
18. 1,1,2-Trichloroethane	
19. Trichloroethylene	
20. Vinyl chloride	

DI PROCEDURE
Inorganics

Waste #_____ RUN #1

Initial separation Required (Circle One) Yes No

If Yes: gm of initial sample filtered _____ gm
gm of total filtrate _____ gm
volume of total filtrate _____ ml
gm of total solid _____ gm

gm of solid leached _____ gm
ml of buffer added _____ ml
ml of filtrate added (if applicable) _____ ml
Initial pH of extract _____ s.u.
Final pH of extract _____ s.u.

Date TCLP Started_____

Parameter	Result mg/L	Date	Sample Prep. Method	Analytical Method #	Analyst Initials
Arsenic					
Barium					
Cadmium					
Chromium					
Lead					
Mercury					
Selenium					

DI PROCEDURE
Inorganics

Waste #_____ RUN #2

Initial separation Required (Circle One) Yes No

If Yes: gm of initial sample filtered _____ gm
gm of total filtrate _____ gm
volume of total filtrate _____ ml
gm of total solid _____ gm

gm of solid leached _____ gm
ml of buffer added _____ ml
ml of filtrate added (if applicable) _____ ml
Initial pH of extract _____ s.u.
Final pH of extract _____ s.u.

Date TCLP Started_____

Parameter	Result mg/L	Date	Sample Prep. Method	Analytical Method #	Analyst Initials
Arsenic					
Barium					
Cadmium					
Chromium					
Lead					
Mercury					
Selenium					

DI PROCEDURE
Inorganics

Waste #_____ SPIKE

Initial separation Required (Circle One) Yes No

If Yes: gm of initial sample filtered _____ gm
gm of total filtrate _____ gm
volume of total filtrate _____ ml
gm of total solid _____ gm

gm of solid leached _____ gm
ml of buffer added _____ ml
ml of filtrate added (if applicable) _____ ml
Initial pH of extract _____ s.u.
Final pH of extract _____ s.u.

Date TCLP Started_____

Parameter	Result mg/L	Date	Sample Prep. Method	Analytical Method #	Analyst Initials
Arsenic					
Barium					
Cadmium					
Chromium					
Lead					
Mercury					
Selenium					

DI PROCEDURE
Semi-Volatiles

Waste #_____ RUN #1 Analyst's Initials

Date TCLP Started _____ _____

Date Acid Extractable Clean-up _____ _____

Date(s) Methylene Chloride Extraction _____ _____

Date(s) of Acid Extractables Analysis _____ _____

Date(s) of Base/Neutrals Analysis _____ _____

Parameter	Result (ug/l)
1. Bis(2-chloroethyl)ether	
2. Cresols (total)	
3. 1,2-Dichlorobenzene	
4. 1,4-Dichlorobenzene	
5. 2,4-Dinitrotoluene	
6. Hexachlorobenzene	
7. Hexachlorobutadiene	
8. Hexachloroethane	
9. Nitrobenzene	
10. Pentachlorophenol	
11. Phenol	
12. 2,3,4,6-Tetrachlorophenol	
13. 2,4,5-Trichlorophenol	
14. 2,4,6-Trichlorophenol	

DI PROCEDURE
Semi-Volatiles

Waste #_____ RUN #2 Analyst's Initials

Date TCLP Started _____ _____

Date Acid Extractable Clean-up _____ _____

Date(s) Methylene Chloride Extraction _____ _____

Date(s) of Acid Extractables Analysis _____ _____

Date(s) of Base/Neutrals Analysis _____ _____

	Parameter	Result (ug/l)
1.	Bis(2-chloroethyl)ether	
2.	Cresols (total)	
3.	1,2-Dichlorobenzene	
4.	1,4-Dichlorobenzene	
5.	2,4-Dinitrotoluene	
6.	Hexachlorobenzene	
7.	Hexachlorobutadiene	
8.	Hexachloroethane	
9.	Nitrobenzene	
10.	Pentachlorophenol	
11.	Phenol	
12.	2,3,4,6-Tetrachlorophenol	
13.	2,4,5-Trichlorophenol	
14.	2,4,6-Trichlorophenol	

DI PROCEDURE
Semi-Volatiles

Waste #_____ SPIKE Analyst's Initials

Date TCLP Started _____ _____

Date Acid Extractable Clean-up _____ _____

Date(s) Methylene Chloride Extraction _____ _____

Date(s) of Acid Extractables Analysis _____ _____

Date(s) of Base/Neutrals Analysis _____ _____

Parameter	Result (ug/l)
1. Bis(2-chloroethyl)ether	_____
2. Cresols (total)	_____
3. 1,2-Dichlorobenzene	_____
4. 1,4-Dichlorobenzene	_____
5. 2,4-Dinitrotoluene	_____
6. Hexachlorobenzene	_____
7. Hexachlorobutadiene	_____
8. Hexachloroethane	_____
9. Nitrobenzene	_____
10. Pentachlorophenol	_____
11. Phenol	_____
12. 2,3,4,6-Tetrachlorophenol	_____
13. 2,4,5-Trichlorophenol	_____
14. 2,4,6-Trichlorophenol	_____

Comments and Observations:

Date:_____ Submitted by_____

_____

APPENDIX F

PARTICIPATING LABORATORY COMMENTS

IT CORPORATION

August 5, 1986

Ms. JoAnne E. Barry
American Mining Congress
1920 N Street, NW, Suite 300
Washington, D.C. 20036

TCLP Evaluation

Dear Ms. Barry:

We are in receipt of your recent memorandum regarding the request for comments on the TCLP Study and are pleased to provide the following summary based on our experience with the equipment and procedure during the round-robin collaborative study. You will note that many of our comments are directed towards shortcomings of the equipment design. Assessment of the methodology and data interpretation are limited at this time.

TCLP Summary

- There is contamination from Ba, B, and Zn from the Whatman filters. Many laboratories are still performing the extraction differently. Filters must be washed with 2 ℓ of acid wash and 2 ℓ of H_2O to eliminate contamination.

- At pH 3.9, chromium values were twice as high as values encountered at pH 5.0.

- Silver and mercury were not extracted under TCLP conditions. Concentrations have been less than the detection limits for these elements.

- The pressure on the vessel should be maintained at the specific pressure and not pushed higher, even if sample remains in the chamber.

- Holding times of the samples must be determined from time of collection to time of extraction, and minimized whenever possible.

- Each lab must determine the dead volume between the screen and valve for each ZHE.
- Labs should put the sample in the middle of the screen and spread rapidly over screen. Care should be taken not to place the sample on the edge of the screen.
- Samples should be kept in cold storage prior to analysis.
- The number of samples that can be processed per day is very limited unless laboratories have several ZHEs and rotary extractors.
- If the sample contains water that has to be removed prior to ZHE extraction, the method for adding extraction fluid is extremely difficult with present equipment design.
- Contamination from particles left behind O-rings after the extraction has caused some problems, especially carry-over for VOAs.
- Valve stems have caused recurring problems by leaking because there are not sufficient threads on the stems to tighten down the top plate.
- The pressure behind the piston often leaks slowly.
- Design of the extraction fluid collection port makes it difficult to use because the Luer lock doesn't fit well.
- A better method needs to be devised for spike solution addition because the needle through the fluid port may hit the screen and filter.
- Laboratories need to check purity of reagents used in the preparation of extraction fluids.
- A see-through top in the extractor would be beneficial to help confirm the presence of air in the ZHE.
- Viton wipers and O-rings seem to wear out quickly.
- Pistons are very tight--physical strength is needed to manipulate the apparatus.

We hope that you will find our comments useful in evaluating the TCLP procedure. Should you have an further questions, please feel free to contact me at our Export Laboratory.

Very truly yours,

Richard M. Burke, General Manager
Laboratory Services

RMB:smr

PEI Associates, Inc.

Ms. Connie Glover
Lancy Laboratories
525 West New Castle Street
P.O. Box 490
Zelienople, PA 16063

Re: PN 4603

Dear Connie:

During this study for the American Mining Congress and the EPA Collaborative study, the TCLP and the ZHE have provided us with analytical dilemmas as well as sample handling problems. These problems are listed below:

TCLP: The extraction itself is not difficult- a technician can perform the extractions without much training. The pH procedure can be tedious, especially if a large number of samples are to be extracted. The extraction vessels that we originally purchased from Associated Design were glass and they broke during the first use. Telfon extraction vessels are better, but do not have a wide mouth, they are expensive, do not clean up very well, and large sizes (3 liter) will not fit into the rotary device. We had a lot of problems fitting containers into the rotary device that are readily available.

The availablity of the Whatman filters is a big problem. Currently, there is a 3-6 week backlog. Another supplier of filters must be found--projects cannot wait 3-6 weeks.

The extracts for the semi-volatiles were "dirty". This included the extraction blanks. There were many peaks and interferences with the pesticide retention time. Our analyst concur that the procedure does not give an accurate indication of contamination. How does the analyst know if the non-detectables are due to the ineffective leaching procedure or if there are no compounds present. Recovery of surrogates is low or not detected. Is this a matrix problem ? This leaching procedure is also being used to evaluate the presence of Appendix 8 compounds in some cases and there are no acceptable analytical procedures. A clear definition of the application of this procedure must be made.

ZHE: The ZHE procedure is in need of re-evaluation. First of all, the sampling will result in a loss of volatiles as well as the particle reduction procedure. By the time the sample is in the ZHE the volatiles are lost. In addition,during the time prior to extraction, the samples settled down resulting in headspace - again a loss as soon as the vial is opened. Sample weighing and loading into the ZHE without loss of volatiles is next to impossible. After this point, why extract? Why not just analyze for total volatiles instead? or at least perform a screen to determine if the extraction is even necessary.

PEI Associates, Inc.

The extractor itself has some problems. The pistons do not move easily- as much as 50 psi were required to move the metal disk dc down. The gaskets do wear out after multiple uses (approx 10) an should be replaced. Cleaning the ZHE is difficult and must be addressed. How does an analyst check for possible carry-over? Blan- extractions? Or is carry-over not a problem? Prefiltration of the sample is not consistent enough. The physical nature of the sample will make prefiltration a problem-gritty samples tear up the filter and clog the screens. The addition of the extraction fluid is next impossible when the screen is clogged.

The level of technician to perform the ZHE extraction is higher than that required for the regular TCLP. The technician must be aware of the potential loss of volatiles and be ready to avoid such pitfalls.

The main concern with the inorganic analyses is the matrix effect on arsenic and selenium when using the graphite furnace. Even using MOAs will not produce reliable results.

The following are some questions that I have concerning these procedures:

Since the ZHE is fairly expensive, what is the anticipated life of t ZHE? This could make the cost of analysis too high for some laborator

How is a multiphasic volatile sample handled without loss?

What parameters must be spiked and then analyzed using MOAs if spike recoveries are poor? Does this include organics?

PEI Associates, Inc. is pleased to have participated in the American Mining Congre Study. We hope that the data compiled from the participating laboratories will be of value in addressing the problems with the new procedures.

Sincerely,

PEI Associates, Inc.

Ida Juris Bennett

Ida Juris Bennett
Inorganic Group Supervisor

RADIAN
CORPORATION

August 6, 1986

JoAnne E. Barry
American Mine Congress
Suite 300
1920 N Street NW
Washington, D.C. 20036

Dear Ms. Barry:

Radian Corporation is honored to have been a participant in the inter-industry study for the TCLP. It was definitely a learning experience which we believe will be beneficial to all those involved. Even though we did not complete analysis of the semi-volatile and volatile portion of the study, each sample was extracted according to the protocol. All problems associated with the study are discussed below.

Radian purchased the Millipore ZHE for TCLP analysis for volatiles. The apparatus is easy to operate, but it has several drawbacks. The air-driven piston often sticks in the barrel and requires up to 30 psi to move it. The ZHE is very difficult to clean, especially with oily wastes. Waste can be trapped in the top o-ring as well as the stainless filter screen. A cleaning methodology should be adapted by the EPA to prevent cross-contamination between samples.

The two samples received for volatile analysis produced gas bubbles during the extraction. Volatiles may be lost during the transfer of the sample from the syringe to the VOA. Also, each of the ZHE received was tested for volume, and each was found to have 2 to 4 mL of non-recoverable "dead space".

Particle size reduction for the volatile analysis should be reviewed and tested. There is no way to size fraction a very hard sample in a Tedlar bag or find a grinder that does not generate heat. Very few laboratories have the capabilities to have this type of equipment at 4°C.

There were no problems associated with the filtering procedure. Oily samples filtered slowly, but that is to be expected with most any filtering media. Pre-cleaned or acid-washed glass fiber filters would be a desirable option so that this step could be eliminated.

8501 Mo-Pac Blvd. / P.O. Box 9948 / Austin, Texas 78766 / (512)454-4797

All analytical procedures were standard methods and required no special training of laboratory staff. Some matrix interferences may be associated with the acetic acid extraction fluids. Analysis by GCMS showed low acid surrogate recoveries and high phthalate values that may be traceable to the clean-up columns.

Sincerely,

J.B. Owens
Laboratory Supervisor
TCLP Inter-industry Study

JBO:tan

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Detailed comments on the TCLP follow the order of the proposed method and are identified by the number of the section of the method they address.

1.1 The method, as proposed, does not determine the mobility of any constitutents present in wastes. Rather, it determines the partitioning of constitutents originally present in a waste matrix between the waste and a simulated municipal landfill leachate. Measurements of mobility require the determination of the change in concentration of a constitutent over time and/or space. Static tests such as the TCLP can measure only the final redistribution concentration of the constitutent in the leach medium under the specific conditions of the test.

A more accurate description of the TCLP would say that, "The TCLP determines the leachate concentration of both organic and inorganic contaminants after redistribution between wastes and a simulated municipal landfill leachate. These data are used in state-of-the-art models to determine the mobility of the constitutents in the groundwater environment."

WRI recommends that the Agency adopt a more accurate description of the method to prevent misunderstandings about what the method really measures.

2.3 The Agency needs to define a compatibility test in more detail. For example, is cloudiness in the mixed solutions a sign of incompatibility; how long should the mixed solutions stand to permit the formation of precipitates or mutliple-phases; if the solutions are mixed at room temperature and no sign of incompatibility develops until the solutions are stored at reduced temperature to prevent

degradation of 'apile organics, are the solutions incompatible: if the mixed solutions evolve gas upon mixing (a carbonate containing initial solution and the acidic leachate),are the wastes incompatibile? This is an important issue because it can result in a doubling of the cost of analysis and an unnecessarily heavy work load on limited laboratory capacity.

The method should not require the separate analysis of solutions which form a precipitate upon mixing for two reasons. First, if precipitates form they should be filtered from the sample through a 0.6-0.8 micron filter prior to analysis. This separation is justified because the precipitate is a reaction product of the buffered leachate and the initial liquid phase/waste pair. The pore fluid in the waste undergoes the same reaction during the leach test and the solid products are removed in the leachate filtration step as insoluble materials. If the initial liquid phase and the final leachate are analyzed separately and the results combined mathematically, the results are biased in that they contain an elemental component from the initial liquid phase which was eliminated from the pore fluid/waste pair by the leach test.

Secondly, if the Agency insists on retaining the method as written, the formation of a precipitate should not preclude the analysis of the combined solutions if a representative sample of the solution can be obtained because the SW-846 methods require sample digestion prior to analysis. This eliminates any analytical problem caused by the precipitate. As before, this will result in considerable cost savings, 50%, and conserve laboratory capacity.

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3.1 The preamble to the method makes the point very clearly that there are analytical problems associated with the application of existing methods to waste leachates. This section, as written, does not acknowledge the Agency's earlier statements that matrix problems exist (i.e. interferences) which are not understood nor discussed in the methods.

This section should be changed to accurately reflect the technical realities acknowledged in the preamble.

4.3.3 The use of stainless steel vessels for the extraction of wastes prior to analysis for inorganic materials should be avoided. The combination of the abrasive nature of the waste and the potentially acidic nature of the extraction fluid may contaminate the leachate with elements from the steel (i.e. chromium). Borosilicate glass bottles should be specified in the method to prevent contamination of the leachate with inorganic materials from the soft glass. The cost differential is small over the life of the laboratory equipment inventory because most labs will wash and reuse the two liter bottles. In addition, borosilicate glass bottles may be cleaned in a muffle furnance at temperatures sufficient to remove all traces of organic material.

4.4 Experience has shown that glass fiber filters lose their integrity whren wet. This makes it impractical to wash the filters prior to use. The method should specify that the filters should be washed after the filtration device has been assembled.

5.0 Note. The Agency has presented no rational for the requirement that the leach reagents need to be made up fresh daily. The requirement that the fluid be checked for impurities and that

method blanks be run as part of the analytical methods provide sufficient quality control on reagent quality. As written, the requirement imposes unnecessarily harsh conditions on the laboratories. If a laboratory feels confident it can produce and preserve the integrity of large volumes of leachate over several days, they should be allowed to do so.

7.0 The Agency states that a 75-100 gram sample of waste will "... insure that there is adaquate extract for the required analyses ...". This is debatable. Until such time as the Agency publishes a complete list of all regulated analytes and approved methods, this statement cannot be supported. Experience with the SW-846 methods for semi-volatiles, metals, pesticides, and herbicides has shown that a total of four liters of solution are necessary to do the complete suite of analysis. The metals can be done with less by a careful analyst. To use less than 1 liter in the other determinations is not wise. It results in less analyte in the final solution and this level is harder to quantitate. The issue of the quantatition limit comes into consideration. Less analyte forces the analyst to work nearer the detection limit and increases the analytical error of the determination.

7.6 The method fails to state how the fluids resulting from the centrifugation are treated. Are they discarded or combined with the expressed fluid from the wastes obtained in step 7.9? If the latter, step 7.16 should be expanded to give an equation that includes the amount of waste originally centrifuged, volume of fluid obtained by centrifugation, amount of waste charged to the extractor as a percentage of the waste originally centrifuged, and the amount of

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centrifuged fluid analyzed (separately or combined) as a percentage of the total fluid obtained.

7.10.2 A precautionary note should be added stating that the drying oven should be vented to a hood or other appropriate device to reduce worker exposure to potentially harmful vapors. Explosion may occur when certain types of organic materials such as polynitroaromatics are taken to dryness. They may explode when the water content is taken below a certain point or when they are removed from the oven and subjected to the friction of being handled or transferred.

7.11 Particle size reduction should be accomplished prior to step 7.5 to avoid sample loss during the grinding step. Moist material will adhere to the particle size reduction equipment. This loss will be hard to measure. Moisture loss will be impossible to measure.

7.12.1 The size of the subsample should be specified. The amount of acid added in step 7.13.3 is 3.5 millimoles. This is equal to 140 mg of sodium hydroxide. Therefore if the subsample is small enough, all wastes can be determined to use extraction fluid #1. The only way to avoid this problem is to decide on a total alkalinity cutoff value for the waste solution generated in 7.12.1. This will addd time and expense to the TCLP.

7.12.3 The specification that the sample is to be slurried for 30 seconds prior to covering with a watch glass serves no valid purpose. It is an unnecessary constraint on the analyst and strict adherence is likely to prevent doing multiple samples effectively. With such a short interval, each sample must be treated individually before going on to the next one. This requirement should be dropped.

7.15.3 The volume of initial fluid expressed from the waste may be insufficient for analysis by SW-846 methods. If so, how must the fluid be analyzed?

8.7 The internal volume of the ZHE should be reduced to approximately 110% of the volume of waste to be charged to the ZHE to minimize the headspace in the assembled device. This will reduce the loss of volatiles when the remaining headspace is eliminated from the assembled ZHE.

8.12 The method requires a prior knowledge of the waste to predict if multiphasic solutions will be created when the initial liquid phase is combined with the final leachate. The TCLP should describe a screening test to guide the analyst in the choice of using a separate filtrate container to hold the leachate.

8.14 Same comment as 7.15.3.

9.1 How long must the data be maintained for review?

9.2 Which extraction fluid should be used when the extractor is checked for memory effects.

9.4 This step should specify if all possible contaminants are analyzed for by the method of standard additions or just the ones found above the method detection limits. How does one go about running VOAs by the method of standard additions? Unless a reliable procedure can be cited, the requirement should be dropped.